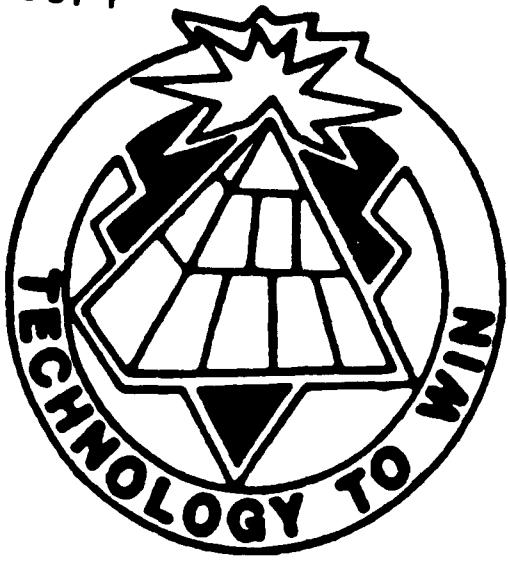


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WORKSHOP PROCEEDINGS

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**CHEMISTRY RELATED TO  
SEMICONDUCTOR GROWTH INVOLVING  
ORGANOMETALLICS**

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JOINT ARO / ETDL WORKSHOP  
FORT MONMOUTH, NJ

G.R. HUSK, K.A. JONES, R.J. PAUR and J.T. PRATER

9-11 MAY 1990

DISTRIBUTION STATEMENT A

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Greetings from the "absent" organizer:

From what I have heard, our meeting related to OMCVD was successful in providing cross-fertilization from various related disciplines. As evidence I cite two participants who have used suggestions from the meeting to upgrade their materials production apparatus to a much cleaner system. I hope that there are other participants who found such readily adaptable suggestions. I feel the multidisciplinary ensemble also provided a great deal of mental stimulation. (It was my loss not to be able to attend.) I hope that this recapitulation of the workshop content will be able to jog memories to useful interchanges at ETDL.

*G. Ronald Husk*

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CONFIDENTIAL

#### ATTENDANCE LIST

## CHEMISTRY RELATED TO SEMICONDUCTOR GROWTH INVOLVING ORGANOMETALLICS

### EXECUTIVE SUMMARY

The U.S. Army Research Office in conjunction with the U.S. Army Electronic Technology & Devices Laboratory sponsored a two and one-half day workshop to review various aspects of semiconductor (III-V and II-VI) growth using organometallic (OM) source gases. This workshop was an interdisciplinary gathering with large contingencies from both the crystal growth and organic chemistry communities. The objectives of the meeting were threefold: 1) to encourage an open exchange of information and ideas, 2) to identify research opportunities that would advance the technology base in the U.S. upon which the Army can draw, and 3) to encourage the establishment of collaborative research programs which effectively utilize the diverse resources and strengths that are dispersed through U.S. industry, university, and Army laboratories.

Organometallics are currently being studied as potential precursor phases for use in the growth of semiconductors by chemical vapor deposition (CVD) and gas-source molecular beam epitaxy (MBE). The use of a gas precursor offers unique capabilities for grading or patterning semiconductor layers, for real-time control of the deposition, and in growing phosphide-based semiconductors. At present a major obstacle to widespread acceptance of this technology lies in the toxicity of the hydride sources. This requires the adoption of elaborate and expensive gas handling and discharge equipment. In addition, gas source growth of semiconductors does not match the layer thickness uniformities and low deposition temperatures currently being achieved by traditional MBE. Thus, MBE currently has the edge in most electronic applications. The exception is in solid state lasers where CVD is producing the superior lasers used in communications and optoelectronic applications.

The development of new gas precursors based on organometallic chemistry is attractive because it opens up the possibility for improvements in three areas: 1) safer gas sources, 2) lower deposition temperatures (for sharper interfaces and deposition of volatile elements),

and 3) photo-active sources (for patterned growth).

Present CVD growth of compound semiconductors relies on the use of toxic group V hydride sources, arsine and phosphine. These pose serious safety concerns. Organometallic sources such as tert-butyl arsine are inherently safer sources; they are less toxic and are usually stored at relatively low pressures. It also appears that the overall quality of materials grown from organometallics is, in general, quite good. Papers presented by Haacke (American Cyanamid), Ballingall (GE) and Jordan (Bell Labs) provided materials and device data on materials grown using various organometallics, which showed the materials to be comparable to those obtained by other methods.

However, before advocating the abandonment of the hydrides it must be noted that there are alternative handling/storage methods under development for arsine or phosphine that can significantly mitigate the risk associated with their use, e.g. on-site electrochemical generation. Though the generators are expensive (around \$40K) these can significantly reduce the safety concerns by eliminating the danger of large volume releases of the gases. This could certainly be a viable alternative in cases where it would mitigate the need for a costly redesign of a CVD reactor system to accommodate the less volatile organometallic sources.

Effluent treatment is another area of increasing concern for the growers. In 3 years, the disposal of As-bearing filters will be prohibited in many parts of the country. It is not clear how the industry will address this issue. One of the highlights of the meeting was a presentation by Bowers-Irons (Technical Research Associates, Inc) on a potential biological route to effluent treatment. It involved the combined use of a proprietary bacteria to solubilize the metals and then duckweed to selectively concentrate the semiconductor species (Ga, As, etc).

To a large extent, organometallics can be tailored to have the properties growers might like, for example, precursors with lower decomposition temperatures and useful photochemical properties. At this workshop, Cole-Hamilton (U of St. Andrews) and Ekerdt (U. Texas) reviewed several different compound and synthesis approaches being pursued in their research on organometallics, MO adduct chemistry and single precursor (compounds which contain Ga and As in a 1:1 ratio)

chemistry, respectively. Basic research on the synthesis of new precursor phases is certainly warranted. The general guidelines for the chemists are: the sources should be of high-purity, have volatilities of several Torr at room temperature and be stable against precracking, but decompose cleanly at the substrate introducing impurities at concentrations below the  $10^{15} /cm^3$  level. Research on photochemical and other nonthermal routes for decomposition of the precursors, both gas-phase and surface activated, would be very useful. Good mechanistic studies should provide the synthetic chemists with useful information for developing new precursors and improved rationales for estimating the likelihood of carbon entrapment.

However, let the individual investigator beware. There are difficult hurdles to be surmounted before a new precursor can actually make it to the marketplace. Producers are not highly motivated to incur the costs associated with bringing new precursors to market. The final demand, and therefore profit, is low, and the risks are high. A major problem appears to be that few of the gas producers in this country have the dedicated growth facilities needed to demonstrate the feasibility of new gas sources. The use of outside facilities is problematical. The cooperative relationship that exists in the UK between industry, government, and academia in this field was held up as a system that works reasonably well. Government efforts that encourage groups to work together, for example by funding cooperative ventures, is encouraged. These efforts are clearly impacted by the lack of standardization in the field. OMCVD is a young field and there is a need for greater coordination among the participants and a need to begin to standardize the reactor designs.

Studies of precursor-decomposition and semiconductor-growth mechanisms are needed, especially as input for the design of improved reactors for better deposition uniformity. The chemistry that occurs in the CVD reactor is extremely complex. There are many examples where the sticking or dissociation rates of one species is affected by the presence of a second species, eg. Ga and In, Cd and Te. Variations due to temperature fluctuations also occur. These effects greatly complicate the calibrations needed to obtain precise control of film composition and growth rate. At least with current precursors much of the decomposition chemistry occurs on the surface of the growing semiconductor. For example, it appears that precursors such as trimethylgallium reach the surface as the di- or trimethyl compound. Thus, while gas phase thermal

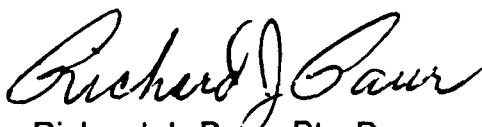
decomposition studies of precursors can provide useful insight, they are probably less valuable than similarly detailed studies of surface reactions. In particular, mechanism studies need to address the trapping of organic fragments in the growing semiconductor and possible methods of efficiently extracting the carbon species to reduce impurity levels to those required for device applications.

In contrast to MBE, where the low pressure environment permits the use of RHEED (and other techniques) to provide in-situ monitoring of layer growth, there are few diagnostic techniques available for use in CVD systems. Three talks were presented on recent developments of in-situ analytical techniques that are available for probing the OMCVD reactions: Aspnes (Bellcore) on reflectance-difference spectroscopy, Pollak (Brooklyn College) on photoreflectance techniques, and Kisker ( Bell Labs) on X-ray scattering techniques. The development of an in-situ monitoring technique for the CVD chamber would be an important step in advancing the technology for future production environments.

In conclusion, OMCVD currently has its niche, but to become broadly accepted two major issues must be addressed. The safety and waste management issues will have to be confronted. The development of new, safer precursors based on organometallic compounds may be a part, though clearly not the whole solution. In addition, the design of the CVD reactors will have to be improved to provide multiwafer uniformity and layer abruptnesses comparable to those obtained with MBE. This is intimately tied to the type of gas source being used and ultimately provides a real disincentive to the substitution of new precursor sources with substantially different properties. Since the industry is unlikely to adopt new materials/technology unless significant improvements can be realized, research which benefits safety or toxic waste management may be the most quickly assimilated due to pending rules governing disposal of waste material from the semiconductor industry.



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Workshop Summary

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The Army workshop, "Chemistry Related to Semiconductor Growth Involving Organometallics", was the first meeting which involved large contingencies from both the organic chemistry and crystal growth communities. It was clear that a coordinated program in selected areas between these disciplines would be required to solve many of the existing problems with OMVPE, MOMBE, ALE, etc. Several technical issues emerged during the workshop and are summarized with comments in the list below:

**1. Safety with Hydrides**

Facility related issues were discussed which results in obtaining the 1/2 IDLH levels for arsine at the point of release into the environment (worst case). Arsine has a 6 ppm IDLH value, 5 times lower than chlorine which is used in very large quantities in water treatment plants.

**2. Hydride Generation**

Two new technologies for the generation of arsine were discussed. These are using chemical and electrochemical cells, both of which presumably require post purification of the arsine prior to use. Questions of water vapor content and overall purity remain, but implementation of either of these methods should dramatically reduce the hazards (or complexity of facilities) associated with conventional OMVPE processes. With both techniques reasonably large quantities of gas are available, but it appears that the electrochemical method produces a more controlled source (pressure and flow). The electrochemical cell also uses reactants (metallic arsenic and electrolyte) that are stable in air. Eventually the prohibitively high cost of these generators will become an issue.

**3. Hydride Substitutes**

The most successful organometallic sources used to replace the hydrides used in III-V compound growth are tertiarbutyl-arsine and -phosphine. These compounds are less toxic and are stored at relatively low pressure. High quality Al free alloys are obtained at high group V/III ratios. These compounds decompose to generate the hydride species in the reaction cell which still requires some level of gas detection and scrubbing in a support facility. It appears that hydride generation offers nearly the same level of safety margin as these approaches, and results in higher quality Al containing alloys.

#### 4. New Organometallic Sources

- a) Trimethylamine Alane - Presently, Galane compounds are unstable; but when used with TEGa, significantly reduced oxygen and carbon contamination results in MOMB E AlGaAs. Possibly, this group of sources will improve the purity of low pressure OMVPE AlGaAs materials.
- b) Organometallic Single Source Precursors - Potentially offers growth of binary and ternary III-V alloys from a single source. Polycrystalline GaAs films have been obtained. Large carbon concentrations were observed. These molecules generally have a low vapor pressure (< 1 torr) requiring low pressure operation of source bubblers.
- c) Photo-Sensitive Organometallic Group III Sources - New Ga source under development which absorbs near 400 nm for photo-enhanced selective growth with an Ar<sup>+</sup> laser. TMGa and TEGa required less than 220 nm radiation to experience photo-enhanced decomposition. There are no high power, coherent sources commercially available in this wavelength range.

#### 5. MOMB E

Process requires low V/III ratios but strong substrate temperature dependence on growth rate. TMGa effectively used for carbon doping; hole concentrations over  $10^{20} \text{ cm}^{-3}$  have been achieved in GaAs. Reasonable quality AlGaAs/GaAs 2DEG obtained using triisobutylaluminum and TEGa. ALE growth mode demonstrated.

#### 6. Carbon Doping in OMVPE

Can be achieved using TMAs, CCl<sub>4</sub>, or by conventional low pressure growth in a plasma. Hole concentrations in excess of  $10^{19} \text{ cm}^{-3}$  have been achieved in GaAs.

#### 7. In-Situ Characterization

Photo-Reflectance and Reflectance-Difference spectroscopies used during OMVPE. The former technique is used to measure the energy bandgap of a bulk grown structure thereby determining alloy composition in-situ. The latter method is a surface sensitive technique, and has been used to determine the monolayer growth saturation time during ALE.

# OMVPE Technology Requirements for III-V Compounds

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## Extended Abstract

There are 2 principle reasons that OMVPE is not in widespread use for the production of compound semiconductor devices. First, the hazards associated with the use of hydrides requires that elaborate facilities be put into place and that the public concern for safety is addressed. Second, at least for AlGaAs based materials, the uniformity of OMVPE structures can not match that of MBE (currently producing less than 1 % variation in thickness over a 3" substrate). The former issue can be addressed by the improved handling of hydrides (which offers nearly ideal chemistry for OMVPE) or replacement of hydrides with organometallic alternatives. The uniformity issue requires better reactor design for both the cell and gas handling system and multi-wafer systems to offer a competitive advantage over MBE.

The OMVPE technique possesses unique capabilities for producing phosphide based semiconductor materials offering epitaxial structures for improved electron confinement for HEMTs, and optoelectronic devices such as visible and IR lasers for communications in free space and with optical fibers. Currently these phosphide materials systems have received relatively little attention for high speed electron devices, and to a lesser extent, optoelectronic devices. Some interesting problems arise in the growth of many of these heterostructures.

In order to be considered a serious candidate for high speed electron devices and integrated circuits, OMVPE must offer comparable uniformity to MBE grown structures and/or superior performance through the use of new heterostructures with phosphide alloys. Furthermore, high quality commercially available reactors such as the case with MBE would help expand the use of OMVPE in production environments. Currently it seems that commercial OMVPE equipment manufacturers do not fabricate 2 machines of the same design. Although OMVPE grown HEMT structures with AlGaAs can match the performance of MBE grown structures, there have been no reports of optimized pseudomorphic AlGaAs/GaInAs/GaAs structures for high performance devices. Progress in the deposition uniformity has been observed on multi wafer systems. Thickness uniformities are approaching  $\pm 1\%$  across multiple 2" substrates<sup>1</sup>. This system is a rotating disk geometry and can handle up to 5 - 3" substrates per deposition run. Also, a multi-wafer horizontal system has produced better than  $\pm 1.5\%$  uniformity in thickness and  $\pm 4\%$  in doping over 3 - 2" diameter substrates<sup>2</sup>. In this study, HEMT structures were produced with the GaInP/GaAs system. This system offers improved electron confinement in 2D electron gases with shallow donor species in the barrier material. Furthermore, GaInP can be prepared with comparable purity to GaAs. The difficulty which arises is the formation of a high quality arsenide to phosphide interface. Due to the interface properties this system has produced LN<sub>2</sub> mobilities significantly less

than the AlGaAs/GaAs system ( $60,000 \text{ cm}^2/\text{V}\cdot\text{s}$ ). However, at large sheet electron concentrations (thin spacer regions) the mobility can actually exceed that of AlGaAs/GaAs structures. If this phosphide system is alloyed with Al (i.e. AlGaInP/GaAs), the effective potential barrier for electron confinement can be doubled (to 0.34 eV) compared to AlGaAs/GaAs. Other systems which should provide high power mm-wave devices include the AlInAs/InP structure which also requires the OMVPE technique.

For optoelectronic devices, in particular semiconductor lasers, OMVPE can find a major role in producing phosphide materials for infrared (1.3 and  $1.55 \mu\text{m}$ ) and visible (640 - 680 nm) laser sources. Currently MBE grown AlGaAs lasers have produced better wavelength uniformity and lower threshold current densities<sup>3</sup>. Recently, optimized GRIN-SCH structures have been prepared with OMVPE grown GaInAsP materials<sup>4</sup> which resulted a  $1.3 \mu\text{m}$  device with a threshold current density of  $\approx 400 \text{ amps/cm}^2$ . Visible semiconductor lasers with AlGaInP materials are currently operating at threshold approaching  $1000 \text{ amps/cm}^2$  for both DH structures (680 nm)<sup>5</sup> and single quantum well GRIN-SCH structures (655 nm)<sup>6</sup>. There are MBE results on visible lasers, but the results are inferior.

There have been several new epitaxial growth technologies to emerge which are derivatives of MBE and/or OMVPE processes. Consider first the use of alternative sources to hydrides in OMVPE. These processes have the advantage of a non-compressed gas source for As and P, but generally result in poorer quality films especially in Al containing alloys. However, recent progress has resulted in reasonably high purity GaAs<sup>7</sup> and InP<sup>8</sup> films. When AlGaAs films were prepared with triethylarsenic, carbon contamination reached the  $10^{18} \text{ cm}^{-3}$  level and the growth rate and Al composition was a strong function of the growth temperature<sup>9</sup>. Metalorganic MBE (MOMBE) processes have been developed where typically solid or hydride group V sources and organometallic group III sources have been used. Due to the lack of excess H<sub>2</sub>, generally severe carbon contamination results using methyl and/or Al containing organometallics. Presently, it is not clear whether MOMBE offers any unique capabilities for III-V materials growth except for heavy p-type doping with C<sup>10</sup>. It is interesting to note that recently MOMBE has produced reasonable purity Al free films using all organometallic sources (hydride free)<sup>11</sup>.

An alternative approach to a less hazardous OMVPE process is to improve the handling procedures for hydride cylinders. Currently, conventional gas cabinets are used to house arsine and phosphine cylinders which are not capable of containing a catastrophic cylinder failure. The table below gives the dilution flow requirements to achieve a concentration of one-half the Immediately Dangerous to Human Life (IDLH) toxicity level at the exhaust stack of a gas cabinet housing the indicated 2 lb. hydride cylinder (100 % concentration). In short, if the gas cylinders containing arsine were used without flow limiting orifices or a catastrophic cylinder failure occurred, it is not practical to provide over 300,000 cfm of dilution exhaust. It should be noted that no arsine installation in the U.S. meets the 1/2 IDLH requirement when a catastrophic cylinder failure occurs. It is feasible to have secondary containment around hydride cylinders in both shipping and operation. A D.O.T. approved pressure vessel would be required for a secondary shipping container. Ideally, this container would have a

small port to sample the gas inside (requiring an exception to the D.O.T. regulation) to determine if the cylinder contained within was leaking. During operation, a pressure controlled N<sub>2</sub> dry box enclosure will contain a spill and provide protection against fire (for phosphine). If a fully charged cylinder erupts, a static vacuum is exposed to the dry box interior to avoid over pressurization. The contaminated dry box gas is then passed through an incinerator capable of scrubbing large concentrations of arsine/phosphine.

**Table 1.** Dilution flow (cfm) required to dilute toxic gas cylinder outfitted with and without flow limiting orifices to a level of 1/2 IDLH.

Toxic Gas	DOT Label(s)	Dilution Flow (cfm)
Arsine	P/FG (no orifice)	333,333
Arsine	3 slm orifice	35,310
Arsine	2 slm orifice	23,540
Arsine	1 slm orifice	11,770
Phosphine	P/FG (no orifice)	10,000

Atomic Layer Epitaxy (ALE) offers interesting possibilities for producing uniform epitaxial structures. With ALE, the substrate is subjected to alternate exposures of organometallic group III flux and group V hydride flux. Under the proper growth conditions ( $T < 500^{\circ}\text{C}$ ) monolayer saturated growth on the TMG exposure cycle has been observed with GaAs. As a result, the growth rate will not experience non-uniformity from variations in TMG mole fraction across the susceptor. Unfortunately, presently ALE suffers from C contamination and does not work well with Al containing alloys. In spite of this, reasonable quality AlGaAs quantum well lasers have been prepared with ALE grown GaAs quantum well active regions<sup>12</sup>.

Flow Modulation Epitaxy (FME) is similar to ALE except the growth is not a self-terminating process. Alternate exposures of group III and group V exposures are used at reduced deposition temperatures ( $T \approx 550^{\circ}\text{C}$  for AlGaAs/GaAs). This process can be conceptualized by considering the group V species to diffuse through one to several monolayers of group III species accumulated on the growth surface. This technique results in improved film quality compared to conventional OMVPE (lower EL2 electron trap concentrations) and reduces the growth temperature requirement<sup>13</sup>. Presently it appears FME will play a role in producing novel III-V structures where low growth temperatures are required.

Finally, deep UV photo-assisted OMVPE growth can potentially result in in-situ sub-micron selective growth. The commonly used organometallic compounds have strong absorption features at wavelengths less than 220 nm. Using a coherent optical source operating in this wavelength regime, interference holographic exposures at low substrate temperatures will result in in-situ grating formation. These structures could be used to produce uniform quantum wire arrays or embedded diffraction gratings for optoelectronic devices. Enhanced growth has been observed using a ArF excimer laser (193 nm) operating at 10 Hz with pulse energies as low as  $10 \text{ mJ/cm}^2$  with TMG and arsine<sup>14</sup>. This process offers exciting possibilities for 2 dimensional control of complex epitaxial films and heterostructures.

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## Chemistry Related to Semiconductor Growth Involving Organometallics

9-11 May 1990  
Electronic & Devices Laboratory  
Fort Monmouth, NJ  
Sponsor: ETDL and Army Research Office

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The main focus of the meeting was on methods to improve current MBE, MOMBE, or MOCVD systems and techniques designed around the properties of the simple, very volatile precursors, including  $\text{Me}_3\text{Ga}$  and  $\text{AsH}_3$  with limited discussion of new precursors or the necessary properties required for them in the production of III-V or II-VI compounds. It was clear from the discussions that the continuing use of  $\text{AsH}_3$  is unlikely because of its very high toxicity and because of the considerable danger in its use. The present equipment, however, is designed to use very volatile compounds, thus making the use of heavier organoarsenic derivatives difficult without major redesign of the equipment used for III-V wafer production. It seems apparent that the same problems apply, although to a lesser extent, for the production of other III-V and II-VI semiconductors which are based on the use of the most volatile derivatives of aluminum, gallium, indium, cadmium, mercury, phosphorous, selenium and telurium.

A limited discussion on new gallium arsenides of the type  $(\text{R}_2\text{AsMR}'_2)$  was presented by Ekerdt. Their group has shown some success in obtaining GaAs from these starting materials, but general acceptance of these compounds as precursors for III-V semiconductors has not been forthcoming.

During the course of the panel discussion additional information was shared concerning the synthesis of a variety of new materials from the laboratories of Wells, of Jones and of Oliver. The variety of materials that are possible has been shown to be very great with the possibility of custom synthesis of new materials containing both the Group III and V or II and

VI elements in the same compound. The stability and volatility of the derivatives can be modified to some extent by careful choice of functional groups attached to the metal and non-metal centers. This can be illustrated by the recent reports of monomeric (2,4,6-trimethylphenyl)<sub>3</sub>Al and by the preparation of compounds which are designed to have specific properties--for example, low thermal decomposition temperatures or specific geometries. The latter can be readily shown, based on the preparation of dialkylaluminum thiolates. With minor modifications in the structure of the thiol, the structure of the metal derivative covers the range--dimer, trimer, tetramer and long chain polymer--with the latter compound dissociating to dimer in the gas phase. The dimer, trimer and tetramer have been characterized only recently by our research group and are obtained by differing substitution on the phenyl thiol. The dimer, (Me<sub>2</sub>Al-SPhf)<sub>2</sub>, is formed from the perfluorophenyl derivative, the trimer (2-methylphenyl-S-AlMe<sub>2</sub>)<sub>3</sub> and the tetramer (2,6-dimethylphenyl-S-AlMe<sub>2</sub>)<sub>4</sub> from the corresponding thiols.

The approach used in the design of these materials can be taken to formulate new precursors for III-V and for II-VI compounds with desirable properties. The limitations, however, are substantial and may require different approaches for the preparation of the final III-V or II-VI materials. Most of the new compounds that can be prepared will have limited volatility, will require the use of either very high vacuum or reasonable temperatures, and even then may give only slow wafer growth or will require some other approach for deposition of the materials--for example, decomposition of a film of the organometallic precursor by thermal or photochemical techniques. The advantages that may result are improved utilization of materials, reduction in the problems associated with hazardous materials, and possibly the ability to obtain new phases/materials. Disadvantages will be the need to develop new methods for wafer production and the ever-present problem of preparing materials of extremely high purity.

***Chemistry Related to Semiconductor Growth Involving Organometallics:***  
***Summary of Chemistry Needs***

Richard L. Wells

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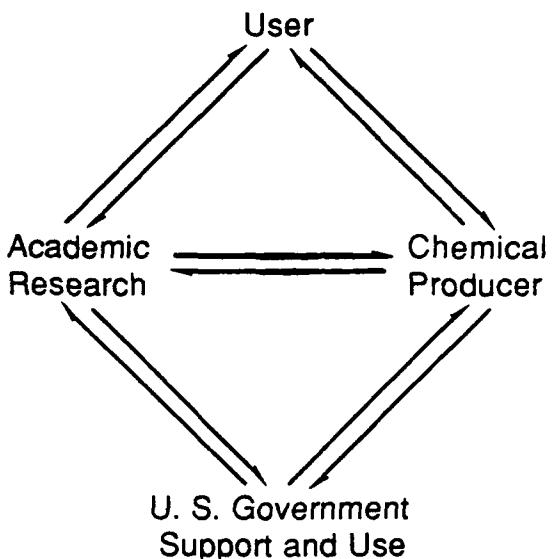
The overall objectives of the workshop, which set the tone and atmosphere for the meeting, were clearly established as a result of succinct statements made by the initial speakers who welcomed the attendees. Briefly stated, the objectives were:

- an exchange of information, including the status of and insight on Army research and currents needs regarding semiconductor growth involving organometallics;
- to identify research required to advance such growth for Army technology; and
- to encourage people to think about technology transfer and joining with Army personnel and laboratories in collaborative research programs.

Throughout the meeting, various speakers and discussants enunciated specific goals and needs which must be addressed, these being:

- in general, a variety of new precursors for II-VI and III-V semiconductor deposition;
- specifically, alternates to AsH<sub>3</sub> and PH<sub>3</sub> as the respective source of arsenic and phosphorus in GaAs and InP, which are less toxic, less sensitive to O<sub>2</sub>, have a lower vapor pressure, readily obtainable in high purity, and will allow a drop in the deposition temperature;
- to decrease the carbon impurities in materials deposited;
- more information on the mechanisms of deposition processes;
- precursors for photochemical growth of semiconductors; and
- experimental reactors to be used in evaluating new precursors.

Assuming that the priorities in precursor chemistry are production, development, and research, there must be collaboration and interaction, as indicated in the following scheme, in order to address these priorities and solve the problems listed above.



One format put forward that could be used to implement the above is the following (*viz.*, the United Kingdom format):

- planning which involves interactions, discussions, and exchange of ideas between growers and chemists;
- funding from government and industry to the growers and chemists to implement the plans;
- cooperation in the form of (a) chemists supplying new precursors to the growers, (b) growers giving relatively rapid feedback to the chemists, (c) chemists supplying alternate precursors to the growers; and
- exploitation in the form of commercialization and sale of materials.

Finally, there was good agreement that workshops such as this one are very valuable for initiating preliminary interactions between a number of people with varied backgrounds, interests, and expertise.

## **WORKSHOP AGENDA**

### **CHEMISTRY RELATED TO SEMICONDUCTOR GROWTH INVOLVING ORGANOMETALLICS**

9-11 MAY 1990

Electronic Technology & Devices Laboratory, Fort Monmouth, NJ  
Sponsors: ETDL and Army Research Office

Wednesday, 9 May, 1990

0730 - 0800 REGISTRATION

0800 - 1200 **SESSION 1, INTRODUCTORY PAPERS**

Session Chairman: Dr. John Prater (ARO)

0800 - 0810	Welcome to ETDL	Dr. Arthur Ballato (ETDL)
0810 - 0820	ARO Welcome and Meeting Objectives	Dr. J. Prater (ARO)
0820 - 0855	Semiconductor Device Requirements	Dr. Ken Jones (ETDL)
0855 - 0910	Army II-VI Deposition Program / MOMB for IR Detector Applications	Dr. Jack Dinan (CNVEO)
0910 - 0955	Epitaxial Growth of III-V's and II-VI's Using Organometallics	Dr. J. Ballingall (General Electric)
0955 - 1025	Break	
1025 - 1100	Device Requirements	Dr. W. T. Tsang (Bell Labs)
1100 - 1135	Environmental and Safety Issues in MOVPE	Dr. R. M. Lum (Bell Labs)
1135 - 1300	Catered Lunch (Possible time for Lab Tour)	

**1300 - 1700 SESSION 2. CHEMISTRY (GAS PHASE) OF III-V SEMICONDUCTOR MATERIALS**

Session Chairman: Dr. Richard Paur (ARO)

1300 - 1335	Chemistry Related to Semiconductor Growth Involving Organometallics	Prof. D.J. Cole-Hamilton (U. of St. Andrews, Scotland)
1335 - 1410	Quantum Chemistry of Vapor Phase	Prof. Art Edwards (UNC-Charlotte)
1410 - 1445	Carbon Doping and Selective Epitaxy: Tailoring Growth Chemistry in MOVPE	Dr. Tom Kuech and Dr. N. Buchan (IBM)
1445 - 1515	Break	
1515 - 1550	TBA/TBP Precursors in GaAs and InP MOCVD	Dr. Gottfried Haacke and S.P. Watkins (Am. Cyanimid)
1550 - 1625	Single Source Precursors for III-V OMCVD Growth	Dr. J. Ekerdt and R. Jones (U. Tx - Austin)
1625 - 1700	Alternate Sources For MOMBE of AlGaAs	Dr. Steven Hersee (General Electric)
1800 -	Dinner on your own or Group Reservations at local Restaurant	

Thursday, 10 May, 1990

**0800 - 1200 SESSION 3. IN-SITU DIAGNOSTICS & THERMODYNAMIC PROCESSES**

Session Chairman: Prof. Dick Shealy (Cornell U)

0800 - 0835	Mechanism of Incorporation of Impurities and Analysis of Carbon Contamination	Prof. G. Stillman (U. Illinois)
0835 - 0910	Growth on Nonplanar and Patterned Substrates	Dr. Raj Bhat (Bellcore)
0910 - 0945	CBE Growth Mechanisms	Dr. A. Robertson (Bell Labs)

0945 - 1015	TriMethylamine Alane: A New Robust Precursor for MOMBE Growth of AlGaAs	Dr. C. R. Abernathy (AT&T Bell)
1015 - 1035	Coffee Break	
1035 - 1110	Real-Time Determinations of OMCVD Growth Kinetics on GaAs by Reflectance-Difference Spectroscopy	Dr. Dave Aspnes, (Bellcore)
1110 - 1145	Photoreflectance Measurements	Prof. Fred Pollak (Brooklyn)
1145 - 1300	Catered Lunch	
1300 - 1700	<b>SESSION 4. II-VI SEMICONDUCTOR GROWTH</b> Session Chairman: Prof. Richard Wells (Duke U)	
1300 - 1335	Growth and Doping Mechanisms for HgCdTe	Prof. Sorab Ghandhi (RPI)
1335 - 1420	Photoassisted CBE of CdTe and HgCdTe Alloys	Prof. Chris Summers (Ga. Tech.)
1420 - 1455	In-situ Analysis of ZnSe Growth by OMCVD Using X-ray Scattering	Dr. D. W. Kisker (Bell)
1455 - 1525	Break	
1525 - 1545	Biodegradation of GaAs IC Chips and Wafers	Gail Bowers-Irons (TRA,Inc)
1545 - 1700	PANEL - NEW PRECURSORS III-V and II-VI	Prof. John Oliver (Wayne St.) Prof. Richard Jones ( U. Tx - Austin) Dr. Duncan Brown (ATM) Dr. George Miller (Am. Cyanimid) Andreas Melas (Morton Int'l)
1800 -	Dinner on your own or Group Reservations at local Restaurant	

Friday, 11 May, 1990

**0800 - 1145 SESSION 5. NEW TECHNIQUES AND PROCESSES**

Session Chairman: Dr. Ken Jones (ETDL)

0800 - 0835	Detailed Models of Compound Semiconductor Growth by MOCVD	Prof. Klavs Jensen (MIT)
0835 - 0910	Gas Phase Probes of GaAs Cluster Chemistry	Prof. Richard Smalley (Rice U.)
0910 - 0945	Photodecomposition of Organometallic Compounds at 193 nm	Dr. W. Braun and Dr. R. Klein (NIST)
0945 - 1020	Manufacturing Issues in MOCVD Compound Semiconductor Technology	Dr. Peter Norris (EMCORE)
1020 - 1040	Coffee Break	

**1040 - 1145 SESSION 6. SUMMARY AND DISCUSSION**

Session Chairman: Dr. Ken Jones (ETDL)

1040 - 1100	Summary of Chemistry Needs and Discussion	Prof. Richard Wells (Duke U)
1100 - 1120	Summary of Technological Needs	Prof. Dick Shealy (Cornell U.)
1120 - 1145	Final Comments & Discussion	Dr. Ken Jones (ETDL)

Adjourn

# **ABSTRACTS**

## OMVPE GROWN MATERIALS STRUCTURES TO MEET THE ARMY'S III-V SEMICONCUDTOR CEVICE REQUIREMENTS

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Areas relevant to this workshop where the Army is focusing its efforts include millimeter wave integrated circuits (MMIC) and devices capable of processing signals at an extremely high rate. Included in the latter are ultrafast devices or arrays of slower devices operating in parallel. Ultrafast device research will focus on nanoscale electronics, mesoscopic devices, and optoelectronics. An example of devices operating in parallel is a focal plane array of optical detectors.

Prominent MMIC devices include the MESFET, HEMT, and HBT. The active layers of these devices must have a uniform thickness to insure that the devices across the wafer have similar properties. Film purity of the layer containing the HEMT channel as well as the spacer layer can strongly affect the mobility of the 2D gas and therefore the device speed. The device speed can also be enhanced by using strained structures such as InGaAs films grown on GaAs. In the HBT a thin heavily doped base is required, but diffusion across the base-emitter and base-collector junctions must be kept to a minimum to optimize the device properties.

QWL's and APD's are important optoelectronic devices, and an important issue for them is the formation of quaternary graded layers which retain lattice matching. The graded composition provides a graded index to more effectively confine the laser light or a graded bandgap to prevent an accumulation of photo-holes at bandgap discontinuities. To provide these optical functions as well as electronic functions on the same chip, mismatched heterojunctions such as Si-GaAs or GaAs-InP junctions might be required.

HgCdTe has been the material of choice for IR focal plane arrays, but there is mounting evidence that GaSb will be a strong competitor if it can be demonstrated that high quality material can be grown.

Another candidate for the IR arrays is the superlattice detector. This mesoscopic device relies on the ability to tunnel through an appropriately biased barrier. There is sufficient time for this to occur only when interface scattering has been reduced to a minimum. Creating smooth, clean interfaces on regrown material will be one of the more challenging problems for structures such as quantum wires and quantum dots that require quantum confinement in the growth plane.

Obtaining films with a uniform thickness will require knowledge of the gas flow patterns. This issue is now being addressed by rotating and revolving the substrate during growth, rotating the substrate at a high speed, using high gas flow rates, and growing at reduced pressures where the boundary layer is thinner. Junctions that are abrupt on an atomic scale are being achieved by employing low growth rates with low reactant partial pressures, high carrier gas flow rates, below atmospheric pressure growth reactors, and low volume, rapid switching valves.

Accurate control of the graded structures will require a more thorough understanding of the growth kinetics and thermodynamics. Issues such as the increased P concentration in GaAsP at higher growth temperatures and the effects on the composition of InGaAsP of changing one or more constituent partial pressure must be addressed. Also, the ability to accommodate strain at lattice mismatched heterojunctions without introducing dislocations and/or stacking faults must be put on a stronger fundamental footing.

Particle assisted growth can be used to lower the growth temperature thereby reducing diffusion across the abrupt junctions. However, this increases the likelihood of impurity incorporation, especially that of C. To avoid this problem, increased knowledge of bond cleavage mechanisms and other decomposition mechanisms such as beta-H elimination reactions is needed. Also, the structures or intermediates as well as their resonances must be determined. Increased knowledge of surface catalyzed reactions is also needed.

Obtaining a better understanding of surface catalyzed reactions could also lead to the improved selective area growth required for quantum confinement in the growth plane. It could also increase the understanding of the growth mechanisms on non-planar substrates.

A final important issue of finding less hazardous substitutes for arsine and phosphine or finding methods to use them in a less hazardous manner must be investigated. The former can be addressed by finding less toxic sources or liquid sources that are dispersed much less rapidly. The latter can be addressed by generating AsH<sub>3</sub> or PH<sub>3</sub> only as it is needed and not storing it at high pressure in a gas cylinder.

Army II-VI Deposition Program - A Rationale for MOMB

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Thermal imagers sensitive to radiation in the 3-5 and 8-12 micron atmospheric windows are required for a variety of strategic and tactical military systems. For the past decade, DOD has sponsored an intensive research program aimed at identifying and developing semiconductor materials, device structures, and processing techniques which result in efficient detection in these spectral regions. Mercury cadmium telluride has emerged as the material of choice and liquid phase epitaxy is now the baseline growth technique. Wet-chemical processing techniques are used to form the two-dimensional arrays that constitute the focal plane. When arrays are fabricated by these conventional techniques, the yield is low and the cost is high. One approach to the solution of this problem involves material growth by a high-throughput vapor phase technique and device processing *in vacuo* by novel dry processing techniques. A rationale is presented for selecting Metal-Organic Molecular Beam Epitaxy as the growth technique in such a scheme. A preview is given of an integrated processing facility based on MOMB which is being assembled at the US Army Center for Night Vision & Electro-Optics.

## GENERAL GROWTH MECHANISMS OF III-V AND II-VI COMPOUND SEMICONDUCTORS USING ORGANOMETALLICS

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III-V compound electronic and optoelectronic device technology has advanced rapidly over the past ten years, largely due to progress in materials, made possible by the development of two sophisticated epitaxial technologies—molecular beam epitaxy (MBE) and metal organic vapor phase epitaxy (MOVPE). Similar advancements are anticipated for HgCdTe as the MBE and MOVPE technologies continue to develop and surpass the performance offered by liquid phase epitaxy for infrared focal plane applications. Metalorganic molecular beam epitaxy (MOMBE) is a relatively new epitaxial technique, derived from MBE and MOVPE, which is expected to make an impact in both III-V and II-VI compound devices.

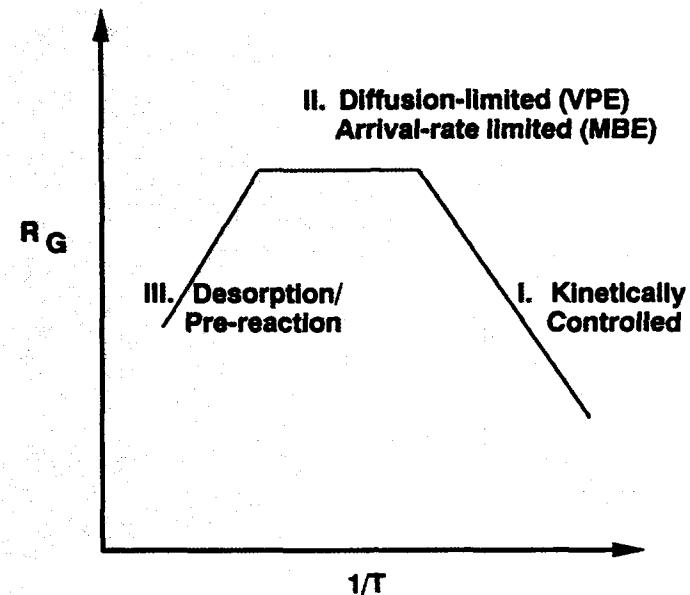
The MOMBE technique is essentially a hybrid of MOVPE and MBE. It combines the principal advantages of both—namely, the mass flow-controlled long-lived sources of MOVPE and the line-of-sight, molecular-flow growth regime of MBE. MOVPE maintains adequate control and reproducibility of gas flows to the growth reactor. But, hydrodynamic problems, such as gas-phase depletion, convection, and turbulence, limit the scale-up and reproducibility of the technology. MBE successfully eliminates all of the hydrodynamic problems by virtue of the vacuum growth environment and the consequent molecular-flow growth regime, but uniformity, reproducibility, and throughput are limited by the elemental sources.

Thus, MOMBE and MOVPE fundamentally differ in respect to the pressure and consequent flow regimes of the growth environment. This is because for typical growth chamber geometries, a pressure of  $10^{-3}$  Torr determines a molecular-mean free path that straddles the molecular-flow and viscous-flow regimes. MOMBE beam pressures are usually in the  $10^{-3}$  to  $10^{-4}$  Torr range, while typical MOVPE reactors operate in the 76 to 760 Torr range. At low pressures of MOMBE, the hydrodynamic problems mentioned above for MOVPE are, of course, eliminated, as is all of the gas phase chemistry encountered in the boundary layer and region of the reactor upstream of the substrate where reagents are injected and mixed. Thus, in MOMBE, the growth is completely controlled by events on the substrate surface. This has strong implications for the chemical precursors best suited for each technique.

Despite these great differences, in general terms, MOVPE and MOMBE growth of both III-V's and II-VI's can be described similarly. Figure 1 shows growth rate vs. reciprocal substrate temperature. Three regions are observed in this idealized plot. Region I is kinetically controlled by adsorption or thermal decomposition of the chemical precursors. Region II has sufficient temperature to overcome kinetic barriers and the growth becomes arrival-rate limited, determined by the beam fluxes in MOMBE, and often limited by diffusion through the boundary layer in MOVPE. Generally, in this region, with an excess of the precursor for the highest vapor pressure atomic component of the solid, the growth will be linear to changes in the arrival rate of the other species. Region III is the high temperature regime where desorption of the precursors, their fragments, or atomic species may occur. Also, at the higher temperatures, convective heating of the gas stream in MOVPE can produce pre-reactions leading to pre-deposition upstream from the substrate and so a drop of growth rate on the substrate.

The binary compounds which form a ternary or quaternary alloy will generally have growth rate vs.  $1/T$  behavior which are different from each other, and different from the idealized behavior of Figure 1. Potentially, this can lead to difficulties in controlling layer thickness and composition over large areas, as the substrate temperature uniformity needed could become impractical. A change in growth rate of 1% in one constituent can lead to a compositional variation  $\Delta x/x$  on the order of 1% and a lattice mismatch  $\Delta a/a$  on the order of 0.01%. Nonetheless, to cite a few examples, compositional uniformity of 1% has been accomplished by MOVPE of HgCdTe over  $1\text{ cm}^2$  samples and 2% achieved over 2-inch diameter substrates.<sup>1</sup> Also, uniformity of 1% has been realized by MOMBE of InGaAsP over 2-inch diameter substrates, using conventional, commercially available MBE substrate heaters with a temperature uniformity on the order of  $\pm 10^\circ\text{C}$ .<sup>2</sup> To our knowledge, this is the best uniformity reported for this important quaternary.

In addition to temperature, pressure also has a strong effect on the growth and so, as mentioned earlier, often determines the best chemical precursors for a particular application. A well studied example is the growth of GaAs with trimethylgallium and arsine. High purity n-type material is achieved readily



**Figure 1. Growth Rate vs. Reciprocal Substrate Temperature**

with MOVPE, whereas heavily doped p-type material results in MOMBE. This is believed to be due to gas phase reactions between the reactants which eliminate methane and so minimize the concentration of adsorbed methyl radicals in MOVPE,<sup>3</sup> contrasted to their disassociation on the surface and the consequent incorporation of carbon into MOMBE films.<sup>4,5</sup> Substituting triethylgallium for trimethylgallium in MOMBE results in high purity p-type GaAs, reducing carbon incorporation by several orders of magnitude, presumably because of the  $\beta$ -elimination process the ethyl compounds may undergo to yield ethylene.<sup>6,7</sup>

While the temperature dependence of growth rate and other aspects of growth with organometallics such as doping and impurity incorporation are generally understood at a phenomenological level, and in some cases can be well controlled, detailed growth mechanisms at the atomistic level largely remain unclear. The large number of chemical reactions possible for even the simplest systems makes theoretical modeling a formidable task. The data being provided by the expanding use of in-situ growth diagnostics

will be a key to elucidating growth mechanisms in the future, as it provides a rational guide to those performing growth model calculations, as well as to those involved in the synthesis of new precursors.

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# Chemical Beam Epitaxy for Opto-Electronic Device Applications

by

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## SUMMARY

The process of chemical beam epitaxy (CBE)<sup>1</sup> has attracted very significant interest recently. Important progress has been made, especially in the preparation of compound semiconductor heterostructures for both electronic and photonic device applications.

While very high quality GaInAs/InP quantum wells have been prepared, in this review, we shall concentrate on some recent results of CBE-grown opto-electronic devices<sup>2</sup>. Very high quality  $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$  epilayers closely lattice-matched to InP,  $\Delta a/a \leq 5 \times 10^{-4}$ , have been reproducibly grown over the entire range of composition ( $y \sim 2.2x$ ,  $1 > y > 0$ ). With  $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$  lattice-matched to InP, which is a very important material for device applications; e.g., FET's, bipolar, p-i-n and avalanche photodetectors, electron mobilities of 10,000-12,000 and 40,000-67,000  $\text{cm}^2/\text{Vs}$  at 300 and 77K with  $n$  in the range of  $5 \times 10^{14} - 5 \times 10^{15} \text{ cm}^{-3}$  are routinely obtained in 2-5  $\mu\text{m}$  thick epilayers. For thick epilayers composition uniformity depth-wise is very important for device applications. Excellent composition uniformity is confirmed by the narrow linewidths of the photoluminescence emitted from the epilayer. It is also confirmed by direct composition measurements using Auger depth-profiling technique.

With such high quality materials and hetero-interfaces, a large variety of optical and electronic devices with very high performance have been grown by CBE. These include GaInAs p-i-n photodiodes, APDs, photoconductive detectors, photo-transistors, GaAs double-heterostructure (DH) lasers, 1.3- $\mu\text{m}$  and 1.5- $\mu\text{m}$  wavelength GaInAsP DH lasers, GaInAs/InP QW lasers, very-low-loss GaInAsP/InP optical waveguides, superlattice optical logic etalons, GaInAs/InP high-mobility two-dimensional electron gas FETs, GaInAs/InP MIS-FETs, very-thin-base (150Å) bipolar, tunneling diodes, distributed Bragg reflector (DBR) laser, Fe-doped InP/InGaAs metal-semiconductor-metal photodetector, etc. In the following we describe the performance of the APDs, DBR lasers, bipolar, and tunneling diodes and Fe-doped MSM detector as illustrative samples.

To date, the structure that has shown the most promise for high frequency operation is the multi-layer InP/InGaAsP/InGaAs separate-absorption-graded-multiplication (SAGM-APD) which consists of an InP multiplication region and a  $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$  absorbing layer separated by a transition region comprised of one or more thin layers

of intermediate-bandgap  $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ . To achieve wide bandwidths without degrading any of the other device characteristics, the wafer parameters (layer thicknesses and carrier concentrations) must be maintained within very narrow tolerances. For example, if the carrier concentration of the multiplication region is  $5.5 \times 10^{16}/\text{cm}^3$ , its thickness must be  $0.55 \pm 0.03 \mu\text{m}$ . This degree of precision and uniformity is difficult to achieve by liquid-phase epitaxy (LPE), particularly in a manufacturing environment. As a result, vapor-phase techniques such as hydride vapor-phase epitaxy, and more recently CBE, have been employed to fabricate SAGM-APD wafers. High performance InP/InGaAsP/InGaAs SAGM-SPDs were grown by CBE. In addition to low dark current (< 150 nA at 90% breakdown), good quantum efficiency (>90% at  $\lambda = 1.3 \mu\text{m}$ ) and high avalanche gain ( $M_0 = 40$ ), these APDs exhibit among the highest bandwidth reported for an APD of any type (8 GHz) and among the highest gain-bandwidth product reported for a III-V compound APD (70 GHz).

Advances in lightwave transmission technology will soon lead to a fuller utilization of the optical spectrum through wavelength division multiplexed and coherent systems. These applications will require good control of semiconductor source wavelength, which places demands on both device design and crystal layer thickness and compositional uniformity.  $1.3 \mu\text{m}$  Distributed Bragg Reflector (DBR) lasers with a hybrid growth employing base wafers grown by CBE, and Fe-doped InP lateral current blocking grown by MO-CVD have been evaluated.

One hundred unmounted lasers were taken from across a wafer with no preselection of any kind, and the lasing wavelength was recorded under 1  $\mu\text{sec}$  pulsed operation. Those lasers which supported two adjacent modes within the Bragg band were assigned a wavelength corresponding to the weighted average of the two modes. No lasers had any mode lasing outside of an  $11\text{\AA}$  widow, except for eight very high-threshold gain peak location with Fabry-Perot modes. Within the remaining 92 DBR devices, the standard deviation in wavelength is  $\sigma \approx 2.7\text{\AA}$ . Considering the  $-18\text{\AA}$  width of the Bragg band and the random phase placement of modes within the band, this is strong evidence of good thickness and compositional uniformity of the crystal growth.

Calculations were performed to estimate the thickness and compositional uniformity required to achieve this level of wavelength control. The thickness or composition of the passive guide layer was perturbed from the values given above, and these perturbed values were then used in a numerical evaluation of the buried heterostructure modal effective index. For example, a  $2.7\text{\AA}$  change in Bragg wavelength will result from a positive waveguide layer thickness change of only  $65\text{\AA}$ , or a compositional change to shift the luminescence wavelength of this layer by only  $74\text{\AA}$ .

To date, most of the HBTs studied have the thickness of the GaInAs base in the range of  $0.1 - 0.2 \mu\text{m}$  and p-dopings  $-1 \times 10^{18} \text{ cm}^{-3}$ . These parameters were chosen to achieve high current gains. The low p-doping level in the base increases the minority carrier diffusion length and hence increases the gain, while the relatively thick base layer is needed for reducing the base resistance. For microwave performance it is desirable to have a thin base layer to reduce the base transit time. To keep the base sheet

resistance at a low value (and hence minimize the base charging time), the base doping has to be increased to  $\sim 5 \times 10^{19} \text{ cm}^{-3}$ . However, at these very high base doping levels the reduced minority carrier lifetime limits the base transport efficiency and thus the current gain if a thick base layer is employed. To increase the current gain of such devices, we investigate the transistor characteristics of DHBTs having a very thin base (150Å) and very high p-doping of  $\sim 5 \times 10^{19} \text{ cm}^{-3}$ . A 200-Å thick GaInAsP ( $E_g = 0.94 \text{ eV}$ ) "grading layer" is also grown between the GaInAs/InP base-collector junction. This effectively reduces the conduction band spike at this hetero-interface, and hence improves the collection efficiency of the electrons injected into the base making it capable of higher current drive over standard DHBTs. Reduction of device dimensions to such short length scales imposes special demands on crystal growth. High quality emitter/base heterojunction diodes require exact spatial placement of the necessarily heavily doped p-n junction at the heterointerface. Chemical beam epitaxy is a suitable method for preparing such sophisticated, high performance GaInAs(P)/InP heterojunction bipolar transistors. Note that these are the first DHBTs having such thin base layers. The important results obtained from this thin-base step-graded DHBT are the greatly improved current gain and maximum current drive capability over the standard DHBTs. In spite of the very high base p-doping,  $5 \times 10^{19} \text{ cm}^{-2}$ ,  $\beta$  was as high as 2500. In addition,  $I_c > 350 \text{ mA} (\geq 4.5 \text{ kA/cm}^2)$  have been obtained. Such current drive capability is higher than that achieved in standard DHBTs with no "grading layer".

With double-barrier structures having 80Å InP barriers and a 50Å InGaAs well a peak to valley ratio as large as 4.3 was obtained at 4.2K. A large series of periodic negative differential resistance (NDR) was also observed in a 50-period GaInAs (150Å)/InP (80Å) superlattice. These NDRs may be interpreted as being caused by the resonant tunneling from the first subband of one quantum well to the second subband of the neighboring well. Such perpendicular tunneling results indicate the perfection of GaInAs/InP heterointerfaces by CBE.

Iron-doped semi-insulating InP is important as current-blockage and isolation layer in stripe-geometry lasers, FETs and integrated opto-electronic circuits. We have prepared Fe-doped InP epilayers by CBE using a thermal atomic Fe-doping beam. Epilayers having high resistivities ( $\geq 10^7 \Omega\text{-cm}$ ) were obtained over a wide range of Fe concentrations. Resistivities as high as  $1.3 \times 10^8 \Omega\text{-cm}$  have been obtained. Such resistivity is almost equal to the theoretical value of  $1.37 \times 10^8 \Omega\text{-cm}$  for intrinsic InP estimated using an InP mobility of  $4100 \text{ cm}^2/\text{V}\cdot\text{sec}$  and an Fe-acceptor level of 0.68 eV.

Using such Fe-doped InP an InGaAs Metal/Semiconductor/Metal (MSM) photodetector with a dark current less than  $1 \mu\text{A}$  was obtained. An Fe-doped InP layer was introduced between the metal and the InGaAs absorbing layer to improve the Shottky barrier height. A breakdown voltage of 30 V was achieved. A DC quantum efficiency of 64% and an impulse response 1/e fall time of 190 ps were measured for a  $20 \mu\text{m} \times 100 \mu\text{m}$  device. The layer structure of our device is very attractive for integration with high performance InGaAs/InP FETs.

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## **Environmental and Safety Issues In MOVPE**

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### **ABSTRACT**

Conventional growth chemistries for deposition of III/V semiconductor thin films by metalorganic vapor phase epitaxy (MOVPE) involve use of arsine and phosphine as the Group V reactants. However, both these hydrides are extremely toxic gases stored under high pressure (200-2000 psi) and present significant safety hazards, both with respect to accidental release of a large volume of gas and to the environmental impact of normal processing and disposal of the reactor waste gases. Use of arsine and phosphine in R&D and manufacturing environments is therefore confronted with a number of safety and regulatory issues. This paper will outline the current status of compound toxicity studies, alternative sources to the Group V hydrides, safe waste gas processing techniques, and evolving regulatory trends.

# FUTURE DIRECTIONS IN PRECURSOR DESIGN AND SYNTHESIS

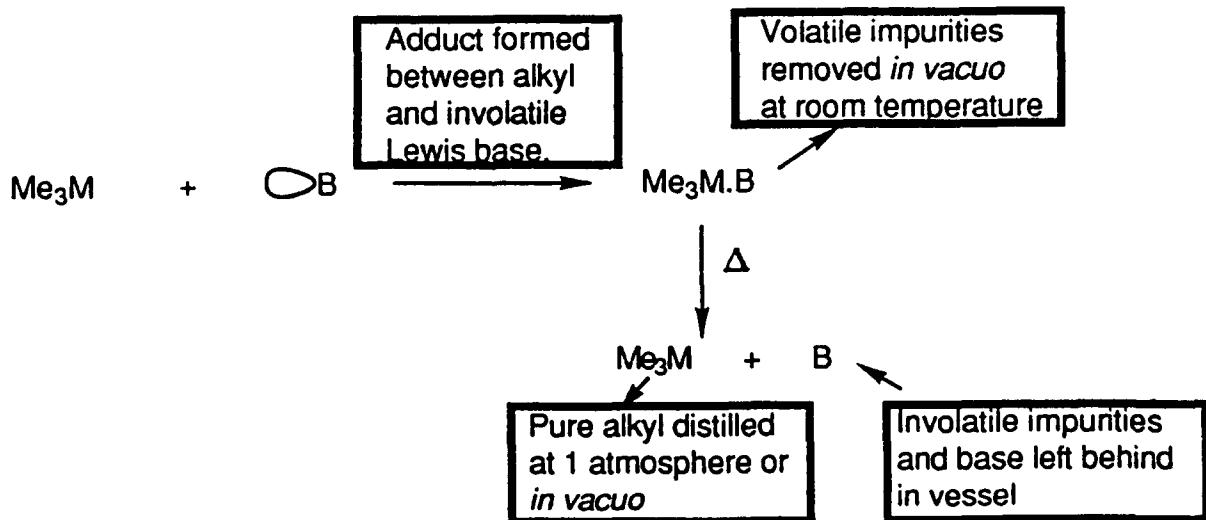
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## EXTENDED ABSTRACT

### Precursor Purification

Much of the recent work on precursor development has been devoted to purifying precursors so that metallic impurities are << 1 ppm. The development of adduct purification, see Scheme 1, has allowed, given careful choice of the correct Lewis Base, the routine purification of relevant alkyls of Gp III, Gp II and Gp VI elements to the desired purity range. Many adduct purified alkyls are available commercially.



Scheme 1

**Scheme 1** Steps involved in the adduct purification process for a group 13 metal alkyl.

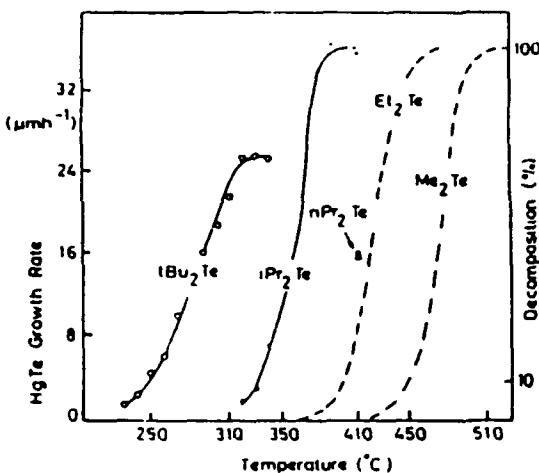
The major problem in this area now is one of analysis and, although Inductively Coupled Optical Emission Spectroscopy has detection limits for many impurities of < 100 ppb, the higher sensitivity of Inductively Coupled Mass Spectrometry means that development of this technique for the analysis of these highly reactive compounds should hold a high priority.

Future research in the precursor area is more likely to involve careful design for precursors to have very specific properties. Some of the areas where this is likely to be important will now be reviewed.

#### Precursors for Lower Temperature Growth

MOVPE growth of compound semi-conductors is generally a high temperature process (300-700°C depending upon the materials system). In all cases there is a minimum temperature below which epitaxial growth will not occur because the mobility of the atoms on the surface is insufficient for complete ordering. However, if the temperature is too high, severe problems occur with diffusion. This can be of dopants or matrix elements either from the substrate or between grown layers in a multilayer structure. This means that interfaces may not be as abrupt as is required and undesired doping may occur. In addition, certain of the elements in the semi-conductors (especially As, P, Hg, S) are volatile and distil from the semi-conductor leaving vacancies. It is often, therefore, desirable to obtain growth at lower temperatures.

As an illustration, Figure 1 shows the effect of altering the alkyl group on tellurium upon the growth temperature for CdTe. Traversing the series Me, Et, <sup>i</sup>Pr, <sup>t</sup>Bu, the growth temperature falls dramatically.<sup>2</sup> Unfortunately, the volatility of the alkyls also decreases across the series so that growth rates from <sup>t</sup>Bu<sub>2</sub>Te can be rather low. <sup>i</sup>Pr<sub>2</sub>Te is currently the favoured precursor for growth of semi-conductors in the cadmium mercury telluride system, but a slightly lower growth temperature would be desirable. A possible approach to this problem is shown in Table 1. Diallyltellurium allows growth at very low temperature but its volatility is quite low. Dimethyltellurium decomposes at a high temperature but is very volatile. Use of the mixed alkyl, (allyl)TeMe, allows growth at low temperatures from a volatile precursor.<sup>3</sup>

**Figure 1**

Comparison of different alkyls showing percentage decomposition for  $\text{Me}_2\text{Te}$  and  $\text{Et}_2\text{Te}$  (broken lines), and HgTe growth rate curves for  $\text{iPr}_2\text{Te}$  and  $\text{tBu}_2\text{Te}$  (full lines). (Reproduced with permission from ref.2.)

**Table 1 Growth temperatures for HgTe from and boiling points of different alkyl-telluriums.**

Alkyl	Growth T/°C	Boiling point/°C
$\text{Me}_2\text{Te}$	500	94 (760 mm)
$(\text{allyl})_2\text{Te}$	180	71 (13 mm)
MeTe allyl	325*	41 (13 mmHg)

\* Hg source is  $\text{Me}_2\text{Hg}$  - controls reaction.

#### Precursors for Low pressure growth

For very accurate control of growth processes; for the formation of highly abrupt interfaces; and for economical use of precursors, it has been shown that growth at low pressures (1 to 10 torr) rather than the usual 1 atmosphere can be helpful. However, it is clear that low pressure growth may require alternative precursors. For example, although  $\text{Me}_3\text{In}$  is preferred over  $\text{Et}_3\text{In}$  for atmospheric pressure growth of InP, using  $\text{Me}_3\text{In}$  for low pressure growth of InP causes significant contamination with carbon, which can be effectively eliminated using  $\text{Et}_3\text{In}$ . These empirical observations suggest different growth mechanisms in

the different pressure regimes and probably mean that reoptimisation of all precursors will be required as the importance of low pressure growth increases.

A special example of low pressure growth is Metal Organic Molecular Beam Epitaxy (MOMBE) in which organometallic compounds replace the more usual elemental sources in a molecular beam apparatus and growth is carried out under conditions of ultra-high vacuum. Optimisation of precursors has not yet been carried out, but a much wider range is possible since much lower volatilities for the precursors can be tolerated. It is possible that single source precursors containing both the elements of a binary semi-conductor (e.g.  $[Me_2GaAs(^tBu)_2]_2$ ) may be useful for MOMBE application.<sup>4</sup>

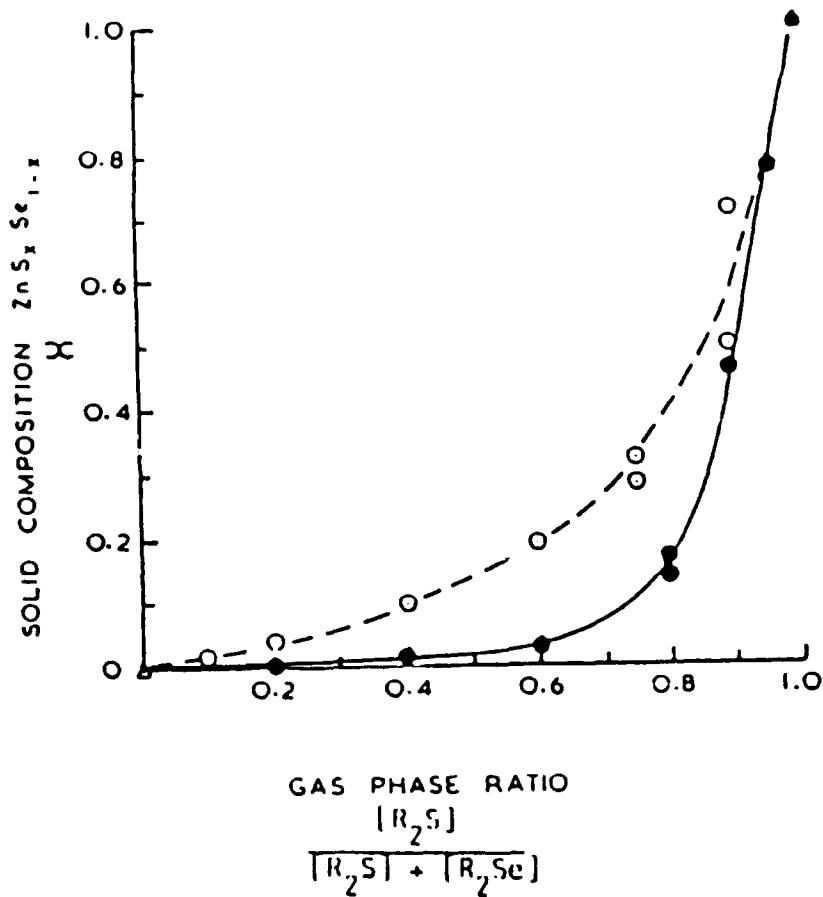
#### Prevention of pre-reactions

In the early days of MOVPE growth of indium phosphide, severe problems were encountered with a pre-reaction between  $Me_3In$  and  $PH_3$  to give an involatile polymer,  $[MeInPH]_n$ . A strategy to overcome this problem was developed which involved the use of a volatile Lewis base adduct of  $Me_3In$ , e.g.  $Me_3In.PMe_3$  or  $Me_3In.NMe_3$ .<sup>5</sup> The Lewis base blocked the pre-reaction but did not appear to interfere with the growth process, being released intact and flushed from the reactor with the effluent gas. It was subsequently discovered that if the  $Me_3In$  was sufficiently pure, the pre-reaction did not occur so this technology has largely been superceded for InP.

The problem does, however, occur drastically in the growth of ZnS or ZnSe from  $Me_2Zn$  and  $H_2S/H_2Se$ , with a shower of amorphous ZnS/Se forming through the reactor. This leads both to depletion of the precursors in the gas phase and hence lack of controllability and to unwanted polycrystalline nucleating sites on the growing surface. This problem has largely been tackled by engineering the reactor so that the precursors do not come into contact with one another until they are close to the substrate, but a more elegant approach may involve the design of precursors such that the pre-reaction does not occur. Preliminary results suggest that adducts with blocking Lewis bases, e.g.  $Me_2Zn.(NEt_3)$  can eliminate the pre-reaction without detrimental effects on growth.<sup>6</sup>

More compatible precursors for growth of ternary and quaternary semi-semiconductors

Although ternary e.g.  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ,  $\text{ZnS}_x\text{Se}_{1-x}$ ,  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  or quaternary e.g.  $\text{Ga}_x\text{In}_{1-x}\text{P}_y\text{As}_{1-y}$  semi-conductors can be grown by MOVPE, the control of their stoichiometry can be very difficult if the two group 16 (15) or 12 (13) precursors do not possess similar breakdown characteristics. Such a situation is shown in Figure 2, where the proportion of



**Figure 2**

% S in a grown layer of  $\text{ZnS}_x\text{Se}_{1-x}$  compared with % S in the gas phase: ● for  $\text{H}_2\text{S}, \text{H}_2\text{Se}$ ; ○ for thiophene, selenophene.<sup>13</sup>

sulphur in grown  $\text{ZnS}_x\text{Se}_{1-x}$  is compared with the proportion of sulphur in the gas phase. Ideally, the curve should be a straight line of slope = 1 through the origin. The stoichiometry of the solid could then be easily adjusted to the required value. Using  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$ , almost

no S is incorporated in the solid up to *ca* 55% in the gas phase and above *ca* 70% very small changes in the H<sub>2</sub>S proportion in the gas phase lead to very large changes in the composition of the solid. Controlling the stoichiometry is thus very difficult. A slight improvement is observed if thiophene and selenophene are used as precursors, although higher growth temperatures are required.<sup>7</sup> There is obvious scope for precursor design in this area.

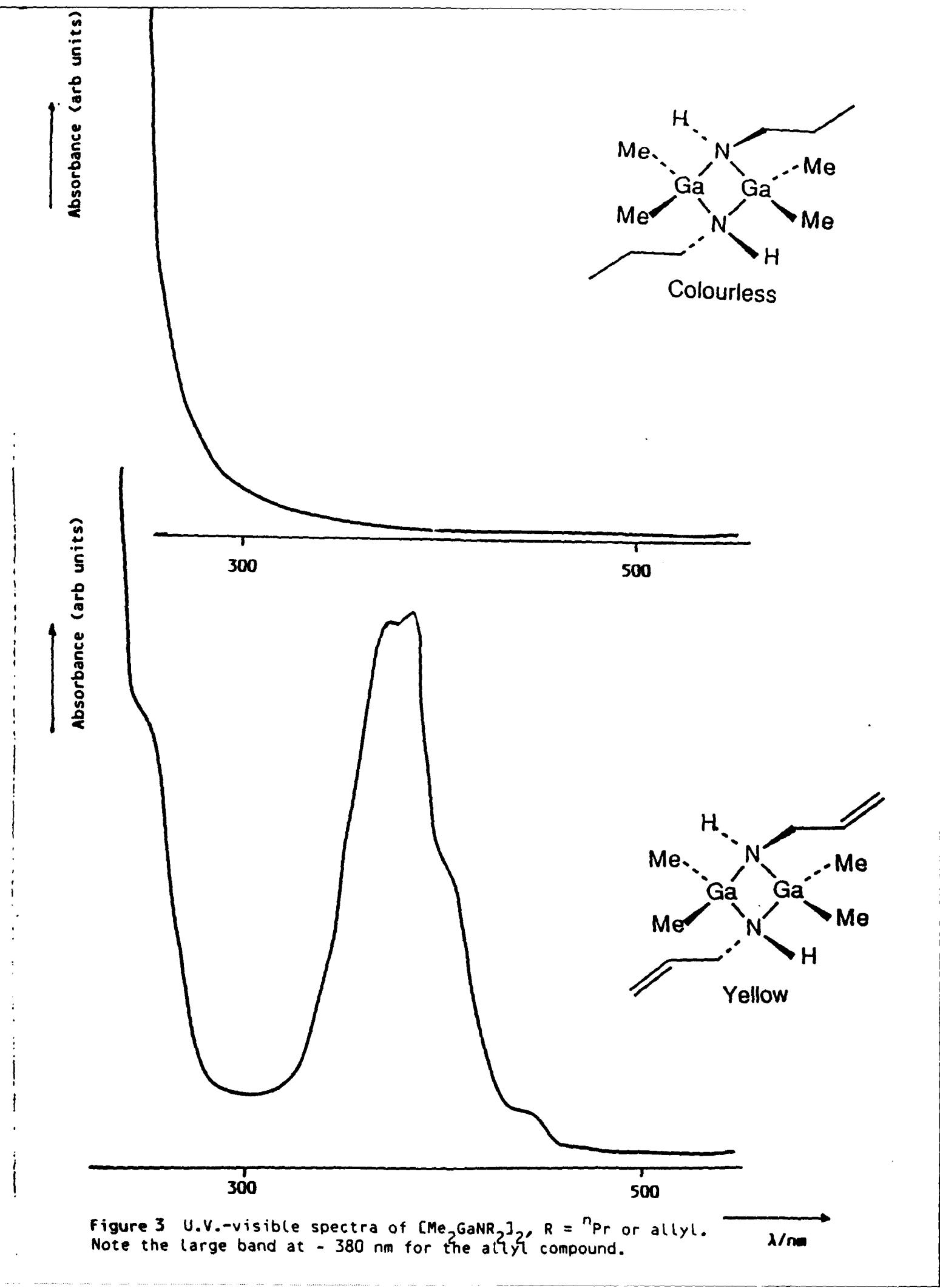
#### Precursors for photochemical growth

Another approach to low temperature growth of compound semi-conductors is to use photostimulation of the growth. Photochemical growth also offers the possibility of complete device fabrication *in situ* by using established masking technology and/or laser writing. Significant progress has been made in the photochemical growth of cadmium mercury telluride and cadmium telluride. In the former the mercury source is metallic mercury and illumination with a mercury lamp promotes deposition at low temperatures (180°C for mercury telluride) apparently by mercury sensitisation. For cadmium telluride, the controlling process appears to be the breakdown of the tellurium precursor and, since these are yellow in colour they have appreciable absorption in the near u.v. region of the spectrum. Laser irradiation at 256 nm promotes epitaxial growth at low temperatures and masks have been employed to produce patterned growth.<sup>2</sup>

The u.v.-visible spectra of two potential Gp 13 precursors are shown in Figure 3. Although the compound containing the bridging propylamide only absorbs in the far u.v., replacement of the propyl group with an allyl group renders the compound yellow and introduces an absorption at 400 n.m.<sup>8</sup> The origin of this absorption is not clear and these compounds have not yet been studied for growth (although [Me<sub>2</sub>GaNMe<sub>2</sub>]<sub>2</sub> has been used for growth of GaAs with AsH<sub>3</sub> as the arsenic source) but it does suggest that introducing unsaturation into the molecules might improve their light absorbing properties.

#### Precursors with safer handling properties

Most of the precursors that are currently used for the vapour phase deposition of compound semi-conductors are either pyrophoric (group 13 metal alkyls, R<sub>2</sub>Zn), highly toxic



(group 15 hydrides, group 16 alkyls) or both ( $R_2Cd$ ). Since MOVPE is already production technology for e.g. GaAs and InP, it is important that the potential risks from the precursors should be minimised. Volatile adducts (see above) are much less reactive in air than the simple metal adducts, but some of their other properties have meant that they have not been widely adopted as precursors.

A possible alternative is to use a dissociable adduct and deliver the metal alkyl by the Modified Entrainment Method (MEM)<sup>9</sup>. This involves delivery via a capillary of known dimensions into a gas stream running across the top of the capillary. The rate of evolution of the precursor is determined only by the temperature of the bottle and the vapour pressure in the bottle. In order to obtain a constant rate of evolution of the precursor from the bottle, it is necessary to employ the dissociable adduct at a temperature below its melting point (since the activity of a solid is 1, whilst that of a molten adduct/Lewis base mixture varies with its composition). Certain adducts, e.g. that of  $Me_3In$  with Arnold's Base, or of  $Me_2Cd$  with 4,4'-bipyridyl, do show appreciable dissociation below their melting points, but even in these cases, the rate of delivery by the MEM method, and hence the growth rate, is very slow.

Attempts to reduce the danger associated with the toxicity of group 15 metal hydrides have largely been based on their substitution by primary or secondary arsines and phosphines. This approach is justified partly because of the lower intrinsic toxicity of these compounds, particularly than of arsine, partly because of their lower volatility and partly because, unlike arsine and phosphine, they can be supplied as neat liquids in bubblers with pressures close to atmospheric rather than as 5-10% mixtures with hydrogen under pressures which are high enough to make a cylinder or line leak a major hazard.

Perhaps the most successful alternative arsenic precursor identified so far is t-butylarsine ( $t\text{-BuAsH}_2$ ) which also has the advantage that growth of gallium arsenide from it and trimethylgallium occurs at lower temperatures than from  $AsH_3$  and  $Me_3Ga$ .

#### Precursors for Mechanistic Studies

Very little is known about the mechanisms of decomposition of metal alkyls or of the growth process, although several different proposals have been made. These include surface

catalysed reactions, free radical decompositions and decomposition of a gas phase or surface Lewis acid - Lewis base adduct.

Carefully designed precursors and experiments will be required to distinguish between various mechanisms but we offer the following very preliminary observations.

E.s.r. studies, which allow the direct detection of free radicals, have been carried out on dialkyl tellurium compounds and it is clear that they decompose, even at room temperature in some cases, to give R· and ·TeR, both of which can be identified. As shown by growth studies<sup>2</sup>, the rate of decomposition is in the order Me<sub>2</sub>Te < iPr<sub>2</sub>Te ~ tBu<sub>2</sub>Te < (allyl)<sub>2</sub>Te ~ (allyl)TeMe. Photochemical decomposition occurs even more rapidly, particularly for (allyl)<sub>2</sub>Te and (allyl)TeMe, although Me<sub>2</sub>Te appears to be stable towards irradiation from a mercury lamp.

In cases where direct e.s.r. studies are inappropriate, we have designed precursors to test whether free radicals are formed or not.

Very preliminary results on the decomposition of 5-hexenylarsine suggest that the major product is hex-1-ene. This shows that the decomposition mechanism does not involve free radicals since the hexenyl radical would cyclise under these conditions to give the methyl cyclopentyl radical and hence methylcyclopentane and methylenecyclopentane, neither of which is observed in appreciable quantities.

### Acknowledgements

My thanks are due to the Ministry of Defence and SERC for support of this work and to my coworkers, D.F. Foster, A.E.D. McQueen, D.V. Shenai-Khatkhate, J. Ferry, and I. Patterson, for allowing me to report their results.

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## Gas-phase Chemistry of OMVPE

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There is a continuing controversy over the importance of gas-phase reactions in OMVPE of III-V semiconductors. Several groups contend that pyrolysis and adduct formation occur in the absence of a semiconductor surface.<sup>1,2</sup> However, other groups hold that surface catalysis is the most important driving force in converting the small organometallic molecules into crystalline solids.<sup>3,4</sup> We have performed a set of molecular orbital calculations on a large set of organometallic molecules to explore the mechanisms of adduct formation in the gas phase. In addition, we hope these calculations start to elucidate the some of the rules for constructing new precursors for OMVPE.

For most of the calculations, we have used *ab initio* techniques employing Gaussian basis sets.<sup>5,6</sup> We have also used MNDO, a semiempirical technique.<sup>7</sup> For each molecule studied we obtained the predicted equilibrium geometry, the associated total energy, and the vibrational spectrum (the last was used for corrections for zero point energy, and for some exploratory calculations of vibrational entropy).

We have reported on a large set of calibration calculations<sup>8</sup> in which we compared calculated and experimental values for equilibrium geometries, energies of atomization, and vibrational spectra. We will not review them in detail here. The theoretical equilibrium geometries for the smaller molecules (TMGa, TMIn, NH<sub>3</sub>, PH<sub>3</sub>, and AsH<sub>3</sub>) are in excellent agreement with experiment. Our calculated III-V bond lengths are systematically larger than those quoted in the literature by about 0.05 Å. Our calculated bondstrengths for heavy atom-hydrogen atom bonds are only fair, while for heavy atom-heavy atom bonds they are quite good, as seen in Fig. 1.

We have studied the adducts formed from TMGa and TMAI reacting with the group V hydrides. Some representative results are shown in Table I. The most striking feature of this table is that the (CH<sub>3</sub>)<sub>2</sub>GaAsH<sub>3</sub> adduct is not bound. Based on simplistic ideas about dative bonds, we might expect very weak bonding, but a net repulsive interaction was most surprising. However, two important features of this molecular system conspire to preclude bonding. First, the lone pair electrons on arsenic are in an almost pure 4s state. This is a fairly compact wave function, with a smaller radius than the 4p states. Second, the As-H bonding orbitals are almost pure 4p states. This leads to closed shell p-charge density that protrudes in front of the lone pair s-orbital forming an annulus. This closed shell charge density can interact with the Ga-C bond closed shell charge density leading to a significant electrostatic repulsion. This repulsion can be reduced if the TMGa takes on a pyramidal geometry. Similarly, the lone pair arsenic orbital could extend further in front of the arsenic molecule, and the extent of the closed shell charge could be reduced, if the H-As-H bond angles would increase (the experimental value for < H-As-H = 92.1°). However, both of these geometrical alterations raise the total energy, so that they only occur if the Ga-As bonding interactions leads to energy lowering that is greater. Clearly, our calculations indicate that the bonding is weaker. These interactions fall under the general category of stearic hindrance.

This argument leads to the following predictions for general trends in adduct bond

strength. 1. For a given group III atom in three fold coordination, the adduct bond strength should decrease as the atomic number of the group V hydride increases. This is due to the increasing radius of the valence p orbitals and hence the increasing size of the protruding p charge cloud on the group V atom 2. For a given group V hydride, the adduct bond strength should increase as the group III atomic number increases, because the radius of the empty p orbital increases leading to greater ease in forming a bond. While prediction one is evidenced beautifully in Table I, prediction 2 seems contradicted. We should point out, however, that the radii of the valence orbitals for aluminum and gallium are nearly identical. However, indium is a much larger atom, so we would expect the In-As adduct to be more stable than the Ga-As adduct. We are presently performing these calculations.

We have also studied the effect of inverting the ligands. That is to say, we have performed calculations on  $\text{H}_3\text{GaN}(\text{CH}_3)_3$ , as well as  $\text{GaNH}_3$  and  $\text{GaN}(\text{CH}_3)_2$ . Results of these calculations are shown in Table II. The hierarchy of bond strengths can again be understood using an argument based on steric hindrance. However, in this case the interactions are not across the adduct bond, but involve the ligands on each side of the ligand bond. The first important observation is that the C-N-C bond angle in trimethylamine is larger than the H-N-H bond angle in ammonia. This is also true for trimethyl-phosphine and -arsine versus phosphine and arsine respectively. The increased bond angle, traceable to increased hydrogen-hydrogen repulsion for hydrogen atoms on different methyl groups, leads to increased p-character in the lone pair orbital, and to diminished p-charge density protruding in front of the molecule. The second observation is that less energy is required to decrease the H-Ga-H bond angle in gallane than to decrease the C-Ga-C bond angle in TMGa for the same reason that the trimethyl amine bond angle increased relative to ammonia. Acting in concert, these two mechanisms increase the Ga-N bond strength dramatically. Furthermore, they cause the  $\text{H}_3\text{GaAS}(\text{CH}_3)_3$  adduct to be bound.

To conclude, we have presented the first calculations of the electronic structure of adducts containing gallium and aluminum. We find that the  $(\text{CH}_3)_3\text{GaAsH}_3$  adduct is not bound. We explain this result in terms of steric hindrance which we believe is a generally, though not exclusively, important concept for understanding adduct bonding. This result may account in part for the reduced importance of gas phase reactions in the GaAs system. However, adduct formation could be important in other III-V OMVPE reactions performed at low temperature where entropic considerations are relatively unimportant.

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## Carbon Doping and Selective Epitaxy: Tailoring the Growth Chemistry in MOVPE

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The metal-organic vapor phase epitaxy (MOVPE) technique is perhaps the most versatile of the conventional III-V growth epitaxial systems. This versatility stems from the wide variety of chemical precursors available for the growth and doping of the films. Two examples of this versatility, carbon doping and selective epitaxy, are presented. Carbon can be incorporated into GaAs from a variety of sources. A comparison study of chlorine and iodine based halomethanes,  $\text{CH}_y\text{X}_{4-y}$ , was presented. The trend in the chloromethanes demonstrates that the weakness of the carbon-halogen bonds, and the number of carbon-halogen bonds, correlates with an increase in incorporation of carbon,  $\text{CCl}_4 >> \text{CHCl}_3 >> \text{CH}_2\text{Cl}_2$ . The series of the iodomethanes demonstrates a different dependence,  $\text{X}_3 < \text{CH}_2\text{I}_2 >> \text{CH}_3\text{I}, \text{CH}_4$ . This decrease in carbon incorporation with higher order iodomethanes suggests that extremely weak carbon-halogen bonds also allows homogeneous gas phase reactions. This systematic change in carbon incorporation with precursor structure provides for a wide range of incorporation characteristics depending on the device application. Carbon precursors suitable for p-type buffer applications would require lower doping efficiencies in order to maintain a high degree of doping control at these low doping levels. Applications involving high p-type doping such as heterojunction bipolar transistors would utilize the more efficient dopant sources.

Selective epitaxy in  $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$  based growth can be also be achieved through tailoring the growth chemistry. Through the use of compounds, such as diethyl gallium chloride and diethyl aluminum chloride the selective area epitaxy of GaAs and  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  can be easily achieved. GaAs can be grown selectively over a wide range of growth conditions which are compatible with the production of high purity materials. The growth process has been thermodynamically modelled in order to estimate relative growth rates and alloy composition. This model indicates that near the growth front the growth process is chemically similar to the inorganic-based growth of compound semiconductors. The

Al composition of the films increases with increasing growth temperature. This is a result of a decrease in the GaAs growth rate due to the addition of HCl from the growth of the AlAs component of the ternary material. The generation of HCl along the gas flow direction, due to upstream deposition, can affect the growth uniformity. This additional HCl will decrease the overall supersaturation near the growth front and result in a lower growth rate. Such influences on the growth uniformity can be mitigated by changes in the growth parameters used in the reactor. Higher gas flow velocities tend to improve the overall uniformity of the growing layers.

Materials properties from selectively grown materials, characteristics of  $(C_2H_5)_2GaCl$  and  $(C_2H_5)_2AlCl$  based growth and properties of selectively grown quantum well structures were obtained. The materials properties of these films are quite similar to those obtained from conventional MOVPE growth on non-patterned substrates. This growth technique has been applied to the growth of extremely low resistance ohmic contact structures and quantum well structures. The interfaces between the selectively grown GaAs and the underlying substrate was found to be free of any substantial concentration of chemical or structural defects. This has allowed the formation of selectively regrown self-aligned source/drain regions required for sub-micron scaled FET fabrication. Selectively grown quantum well structures have been made and the photoluminescence spectra obtained at low temperatures. The PL peak width is broader in the selectively grown structures. This is attributed to the variations in the film thickness near the pattern edge.

## Performance of TBA/TBP Precursors in GaAs and InP MOCVD

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The use of arsine and phosphine for the growth of GaAs and InP epitaxial layers by metalorganic chemical vapor deposition (MOCVD) is receiving increasing public scrutiny. The extreme toxicity of arsine and phosphine, which must be stored in high-pressure steel cylinders, could lead to catastrophic consequences in case of an accidental release of a large quantity of these gases. In such an event, continued use of arsine or phosphine may be prohibited and the supply of GaAs/InP-based military devices could not be guaranteed.

Low-vapor pressure liquid arsine/phosphine derivatives, which avoid the risks and hazards associated with the use of the hydride gases, have been under investigation over the past several years. For some, unacceptable carbon acceptor concentrations, due to intrinsic source chemistry, have been reported in MOCVD studies. For other sources, high background impurity concentrations were observed and it is not yet clear whether economic purification techniques can be worked out or whether the intrinsic chemistry of these sources is adequate to achieve semiconductor-grade purity. In the case of tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP), synthesis and purification technologies have been developed which consistently yield products of high purity.

Semiconductor-grade TBA and TBP are now available in commercial quantities. Both compounds are liquids which have convenient vapor pressures for MOCVD operations. They are stored and transported in stainless steel bubblers approved by DOT. The bubblers can be easily connected to MOCVD reactors following the same procedures customarily used for connecting bubblers containing Group III metalorganics. Extensive in-house MOCVD growth investigations showed that TBA and TBP are fully qualified replacement sources of the hydrides for the MOCVD of III-V semiconductors.

Growth experiments with TBA were carried out in a vertical, 3-inch diameter quartz reactor. Nominally undoped GaAs epitaxial layers were

grown either at atmospheric pressure or at 76 Torr using as Group III source trimethylgallium (TMG) or triethylgallium (TEG). InP growth was performed in a horizontal quartz reactor at 100 Torr pressure. The precursors were TBP and trimethylindium (TMI). Each reactor was dedicated to the respective Group V source and great care was taken to maintain the equipment under ultra-clean conditions. No dopants were introduced into the systems. For the Group III sources only materials of the highest available purity were used.

Growth of GaAs layers at 760 Torr using TBA/TMG showed that over a wide range of growth conditions only p-type GaAs could be obtained. In contrast, GaAs grown under similar conditions with arsine/TMG was n-type having 77K mobilities larger than 100,000 cm<sup>2</sup>/Vs. Low-temperature photoluminescence (PL) and magneto-PL (MPL) spectroscopy demonstrated that the observed differences in Hall properties were caused by differences in the background impurity level of the Group V sources. Commercial arsine contains various concentrations of a germanium species which provides germanium donors to the GaAs. The trace levels of residual donors in commercial TBA are so low that n-type GaAs can not be grown when TMG is used which also has extremely low levels of background donor species. The same TMG bubbler was used for all of the GaAs growth runs.

GaAs growth using TEG always resulted in n-type layers for both Group V sources. The source of the donor impurity was traced to the TEG which contains a low level of a tin and possibly also of a silicon compound. Most of the TEG/TBA and TEG/arsine growth investigations were carried out at 76 Torr. Atmospheric pressure growth showed that under these conditions side reactions between TEG and the Group III compounds occurred which resulted in higher impurity incorporation and made it difficult to achieve good morphology. At 76 Torr, excellent GaAs layers were grown and no difference was found in the properties of TBA- and arsine-grown layers. The measured 77K mobilities were as high as 160,000 cm<sup>2</sup>/Vs and the residual donor and acceptor concentrations were in the E13 - E14 cm<sup>-3</sup> range.

Growth of unintentionally doped InP using TBP/TMI demonstrated that under optimized growth conditions high-quality epilayers could be obtained. The highest 77K mobility observed to date was 130,000 cm<sup>2</sup>/Vs and the residual donors were close to E14 cm<sup>-3</sup>.

SINGLE SOURCE PRECURSORS FOR III-V OMCVD GROWTH:  
FILM GROWTH AND PYROLYSIS STUDIES

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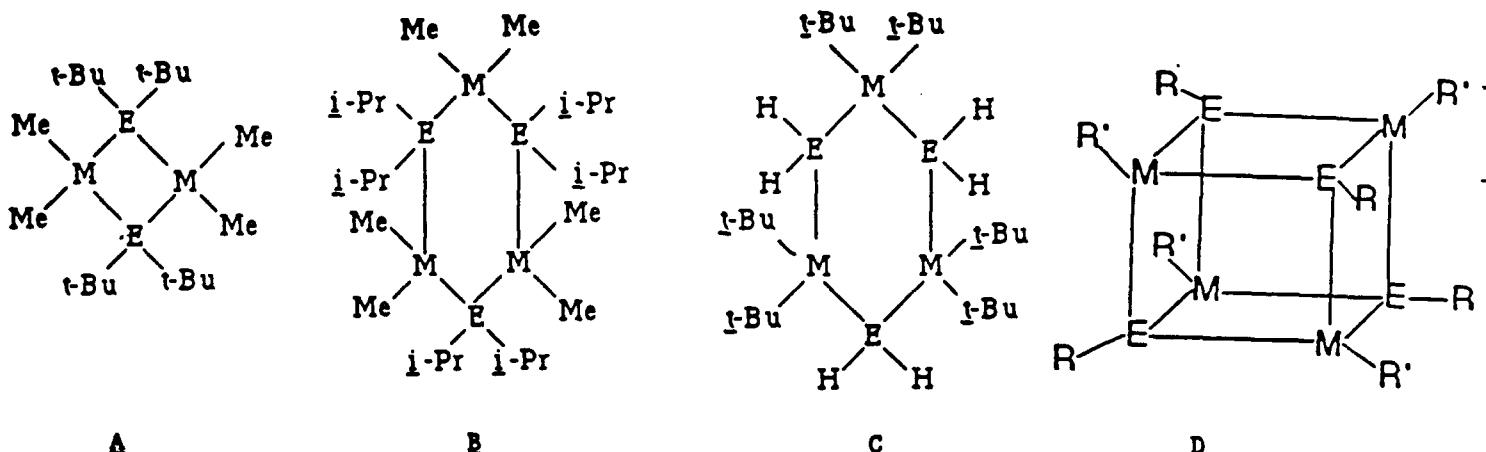
ABSTRACT

Compound semiconductor devices are typically constructed using heterojunction, multi-material structures, e.g., AlGaAs/GaAs heterojunctions. The desire to develop thinner and thinner three-dimensional structures with smaller and smaller lateral dimensions, while maintaining precise control of doping and composition to achieve specified optical and electronic properties, drives much of device research. Many scientific and engineering challenges are associated with further reductions in the sizes of devices and with developing sharper definitions between interfaces. Not only will these developments lead to increased speed and improved performance, but it is also likely that more sophisticated combinations of these compounds will result in unique optical and electronic properties.

Solutions to these challenges - devising new methods and structures, and improving existing ones - will require research on the relevant chemistry as well as the physics and engineering involved in the growth of materials and structures with desired properties. Current methodologies and materials have a number of limitations with respect to low temperature growth ( $T_g < 500^{\circ}\text{C}$ ), localized epitaxial growth, multicomponent compound semiconductors employing quaternary and pentenary alloys, and safety and toxicity issues. One major opportunity for the long-range improvement of commercial organometallic chemical vapor deposition (OMCVD) technology lies in the use of new precursors in chemical vapor deposition (CVD) crystal growth; new precursor chemistry forms a central theme of our program. Specifically designed, novel, single-source precursors are synthesized with varying structures and leaving groups. The thermal stabilities of the precursors are studied in order to effect selective or total ligand loss as a function of temperature and pressure. Films are grown in a CVD reactor to determine how precursor structure influences the decomposition reactions and film properties. Finally, collaborative surface studies are performed to determine the adsorbed structures and surface reactions. The principal objective of our work is to achieve precise control of the physical and electronic properties of semiconductor thin films through the rational design and synthesis of precursors.

Our single-source precursors are of the general type  $(\text{L}_n\text{MEL}_{n'})_x$  and feature the desired 1:1 stoichiometry of the group III (M) and group V (E) elements. Our strategy is to cause the M-E bonds to be as strong as, or stronger than, the other bonds in the cluster by employing two-center, two-electron ( $\sigma$ ) bonds rather than the donor-acceptor linkages found in adducts. We also use ligands, L and L', which are capable of facile hydrocarbon elimination.

At this point, four types of precursor (**A-D**)



have been synthesized and characterized. Compounds of type **A** are prepared in very high yields utilizing a convenient one-pot procedure in which the metal trichloride is treated with one equivalent of  $t\text{-Bu}_2\text{ELi}$  ( $E = \text{P, As}$ ) and two equivalents of  $\text{RLi}$  ( $R = \text{Me, } n\text{-Bu}$ ). A similar procedure can be employed for the synthesis of the trimeric isopropyl-substituted derivatives of type **B**. Precursors of type **C** have been prepared in high yields via the reaction of  $\text{Bu}_3\text{M}$  with  $\text{PH}_3$  or  $\text{AsH}_3$  at low temperatures. Precursors of type **D** have been prepared via the two-step reaction of  $(i\text{-Bu})_2\text{AlH}$  and  $(\text{Ph})_3\text{SiPH}_2$  at  $25^\circ\text{C}$  to form a dimer and then under reflux in toluene to form the tetramer.

Representative examples of compounds of types **A**, **B**, and **C** have been characterized by X-ray crystallography. The  $M_2E_2$  rings of the type **A** compounds  $[\text{Me}_2\text{Ga}-\mu\text{-As}(t\text{-Bu})_2]_2$  and  $[\text{n-Bu}_2\text{Ga}-\mu\text{-As}(t\text{-Bu})_2]_2$ , for example, are planar and the M and E atoms adopt approximately tetrahedral geometries. The conformation of the  $M_3E_3$  ring of the type **B** compound  $[\text{Me}_2\text{Ga}-\mu\text{-As}(i\text{-Pr})_2]_3$  is best described as being of the distorted boat type. Interestingly,  $[\text{t-Bu}_2\text{Ga}-\mu\text{-PH}_2]_3$ , a type **C** compound, adopts a planar  $M_3E_3$  ring conformation. Finally,  $[i\text{-BuAlPSi}(\text{Ph})_3]_4$ , a type **D** compound, adopts an AlP-cubane structure.

In general, compounds of types **A-D** are crystalline solids that are amenable to purification by recrystallization and zone refining techniques. They may be handled in air for short periods of time; however, it is preferable to perform all manipulations in *vacuo* or under an inert atmosphere.

The OMCVD studies with  $[\text{Me}_2\text{Ga}(\mu\text{-i-Pr}_2\text{As})]_3$  (**1**) and  $[\text{Me}_2\text{Ga}(\mu\text{-t-Bu}_2\text{As})]_2$  (**2**) are the most complete. Film growth was studied over the temperature range of  $450\text{-}600^\circ\text{C}$  and at  $10^{-4}$  Torr. Growth rates of  $1\text{ }\mu\text{m/hr}$  are typical when the compounds are maintained at  $125\text{-}140^\circ\text{C}$ . Chemical analysis (SIMS and XPS) of the films revealed that the films did not contain any more carbon than the substrates, indicating ligand loss was complete. Photoluminescence (PL) results (5K) of films grown from **2** showed the band edge at  $1.43\text{ eV}$ , but that the films contained considerable defects. The PL results suggest 1:1 stoichiometry was retained in films from **2**. We suspect the defects were associated with the crystalline properties. Films grown from **1** were milky in

appearance, indicative of a loss of stoichiometry.

The crystalline properties of the films from 2 are very interesting in that a (111) orientation is always favored. Pole figure analysis indicates that (111)-oriented and polycrystalline films were grown over  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) and GaAs(100). The presence of a "ring" of poles at the 70.5° tilt angle indicates that the sample contains grains oriented with cylindrical symmetry along the normal to the sample plane much like a fiber texture. When the As substituents were changed from t-Bu to i-Pr (compound 1) the films still retained the (111) orientational preference; however, the X-ray diffraction peaks for the (220) and (311) planes became more pronounced relative to the (111)-peak intensity.

Pyrolysis experiments were conducted at 10<sup>-4</sup> Torr to study the decomposition pathways of 1 and 2. Several different mechanisms,  $\beta$ -H elimination, intramolecular reductive elimination/coupling, and intermolecular coupling occur. t-Bu ligand loss was observed to occur 50-70°C lower than i-Pr ligand loss. The onset of t-Bu ligand loss occurred at 320°C. Methyl ligands appear to react at 370-500°C. The decomposition of [Me<sub>2</sub>Ga( $\mu$ -t-Bu<sub>2</sub>As)]<sub>2</sub> appears to occur through units no smaller than monomers, Me<sub>2</sub>GaAs(t-Bu)<sub>2</sub>, while [Me<sub>2</sub>Ga( $\mu$ -i-Pr<sub>2</sub>As)]<sub>3</sub> appears to undergo fragmentation to gallium containing species and arsenic containing species.

Our results strongly suggest that it may be possible to control the key materials property of crystalline orientation, through the chemical structure and reactivity of the OMVCD precursor molecule. We suspect that the dimer 2 did not completely dissociate, either during sublimation or following adsorption, to Ga and As because one would expect (100) oriented films on GaAs(100) substrates or polycrystalline films, rather than the (111)-oriented films which we have observed. If Ga-As monomer units adsorb, the orientation of the monomer with respect to the surface normal could direct growth and may explain the preference for (111) oriented films. The manner in which the monomer is adsorbed may be influenced by the ligands remaining on Ga and As. Finally, the reason for fiber-like growth could be related to film nucleation at multiple sites, with a coalescence of nucleated sites occurring after large domains of crystals with the (111) axis normal to the surface have formed.

# ALTERNATIVE SOURCES FOR THE GROWTH OF MOMBE ALGaAs

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## ABSTRACT

This paper describes recent results from an ongoing study of the MOMBE growth of AlGaAs using different aluminum sources.

We compare the growth behavior and properties of AlGaAs grown from triethylaluminum (TEAl), triisobutylaluminum (TIBAl) and the adduct, trimethylamine alane (TMAl).

Electrical and photoluminescence (PL) properties of these layers will be described.

In the case of TEAl and TIBAl the layers are p-type due to the incorporation of residual carbon from the organic radicals. We find that the highest purity AlGaAs is grown from triisobutyl aluminum. Acceptor concentrations in the low  $10^{18}$  cm $^{-3}$  range are readily obtained and Al $_{0.25}$ Ga $_{0.75}$ As mobilities are close to those obtained by MBE growth. In addition, we observe bound excitons in the PL spectrum of the AlGaAs. To our knowledge, this is the first time that bound excitons have been reported for MOMBE grown AlGaAs.

We will discuss the use of mass spectroscopy (MS) during MOMBE growth to obtain information on reagent decomposition.

Comparing MS data for TEAl and TIBAl, we find that TIBAl is apparently more likely to undergo beta elimination than TEAl. While this result is unexpected from simple chemical bond theory, it is consistent with the lower carbon incorporation observed for AlGaAs grown from TIBAl.

# Mechanism of Incorporation of Impurities and Analysis of Carbon Contamination in MOCVD InP<sup>1</sup>

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**ABSTRACT:** Intentional C doping of low pressure MOCVD-grown InP has been attempted. Using mixtures of 500 ppm and 1500 ppm CCl<sub>4</sub> in high-purity H<sub>2</sub> for the C dopant source, C acceptor concentrations as high as  $4 \times 10^{19}$  cm<sup>-3</sup> have been achieved in GaAs. Under growth conditions similar to those used for heavy carbon incorporation in GaAs, injection of CCl<sub>4</sub> into the growth reactor during the growth of InP did not produce any measurable change in the carrier concentration of the InP epitaxial layers or result in any change in the <sup>12</sup>C concentration above the <sup>12</sup>C background level in secondary ion mass spectroscopy (SIMS) analysis. There is no evidence that the group IV impurity C is incorporated in InP grown with common epitaxial growth techniques.

## 1. INTRODUCTION AND BACKGROUND

Carbon is a very important residual acceptor in GaAs grown by various techniques, and in spite of early reports that C is a particularly effective scattering center in GaAs at room temperature (Stringfellow and Kunzel 1980), it is currently also of interest as an intentional p-type dopant in MOCVD and MBE epitaxial growth because of its low diffusion coefficient, compared with Group II p-type dopants which substitute on the Ga sublattice. Carbon is also interesting because, although it is from Group IV of the periodic table and thus is potentially amphoteric in GaAs, InP and other III-V compounds, it is only incorporated as an acceptor in GaAs; i.e., C is not incorporated on the Ga sublattice in GaAs. Carbon is particularly important for growth techniques based on metalorganic compounds since it is an intrinsic impurity in these source materials. In this paper, we review the evidence for identification of C acceptor impurities in InP using photoluminescence (PL) and discuss some potential experimental complications in PL identification of C acceptors in InP. Experiments in which we attempted intentional doping of low pressure MOCVD InP with CCl<sub>4</sub> under conditions similar to those which result in heavy carbon doping of GaAs are described. The results of these experiments support the conclusion that C is not incorporated in MOCVD InP.

<sup>1</sup>Most of the data in this paper was presented at the International Symposium on Gallium Arsenide and Related Compounds, Karuizawa, Japan, 1989

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## 2. IDENTIFICATION OF C ACCEPTOR LEVELS IN InP

Skromme, et al. (1984) have studied the identification of acceptor impurities in InP by measuring the acceptor luminescence in undoped InP grown by LPE, PH<sub>3</sub>-VPE and LEC techniques and in intentionally doped material prepared by C, Be and Mg ion implantation into bulk crystals and epitaxial layers. The dominant residual acceptor in LPE InP was first reported by Hess, et al. (1974) and labelled A<sub>1</sub> by these authors. Although this acceptor has been widely assumed to be C, Skromme, et al. (1984) demonstrated that the energy of the A<sub>1</sub> residual acceptor did not match that of C, as determined from PL measurements on carbon implanted and annealed epitaxial and bulk InP samples. The PL spectra, at four temperatures, of an undoped LEC InP sample implanted with <sup>12</sup>C from Skromme et al., (1984) are shown in Fig. 1. Before implantation, the LEC material contained only residual A<sub>1</sub> and, in much smaller concentrations, Zn acceptors. After <sup>12</sup>C implantation and annealing, the C and A<sub>1</sub> acceptor related PL transitions were of nearly the same amplitude while the donor-to-acceptor transition due to Zn acceptors could not be resolved from the much more intense C (D°-A°) peak. The observation and temperature dependence of the four (D°-A°) and (e - A°) transitions in Figure 1 clearly indicate that the unknown acceptor denoted as A<sub>1</sub> is not C. Comparison of these and other spectra with those of Be and Mg implanted samples indicated that the energy of the A<sub>1</sub> acceptor is the same as that of Be and Mg acceptors. (Within experimental error, all three of these acceptors have the same ionization energy. Comparison of the <sup>12</sup>C implanted InP with a large variety of undoped InP samples grown by LPE, PH<sub>3</sub>-VPE, and LEC techniques indicated that C is not detected as a residual acceptor in InP grown by these techniques.

Recently, high purity MOCVD InP has become available, and the residual impurities in undoped, low pressure MOCVD InP grown with both TMIn and TEIn metalorganic sources have been studied (Uwai, et al. 1987).

The most common residual donor impurities in MOCVD InP are Si and S (Lee, et al. 1989 (a)), and Zn is commonly detected as the dominant residual acceptor species in MOCVD InP (Armistead, et al. 1984), (Bass, et al. 1983), (Zhu, et al. 1985), (Bose, et al. 1989). Some workers have also reported the presence of residual carbon acceptors in MOCVD InP (Bass, et al. 1983, Zhu, et al. 1985), but in light of the results of Skromme, et al. (1984), the identification of carbon by Bass, et al. (1983) is not correct, and the identification of C acceptors by Zhu, et al. (1985) is also doubtful because of their poorly resolved PL spectra and also because of possible misidentification of the PL peaks at high excitation intensity, as described below.

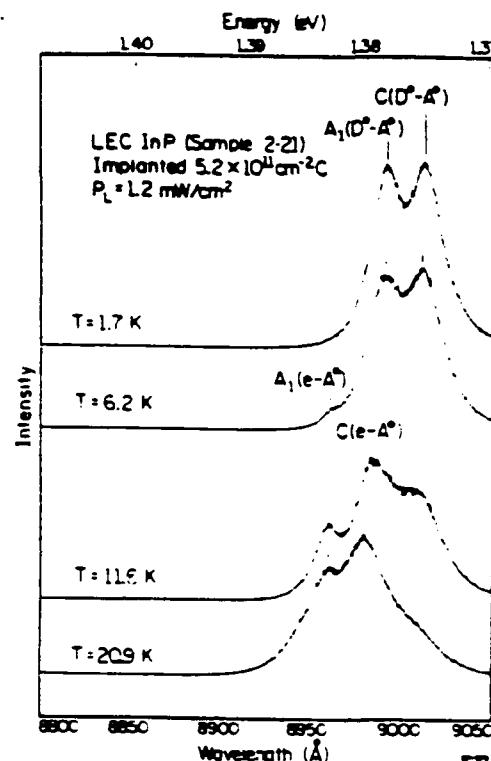


Fig. 1 Temperature variation of PL spectra of an LEC undoped InP sample after a low dose implantation with <sup>12</sup>C and annealing in forming gas at 730°C for 30 minutes with phospho-silicate glass encapsulation, from Skromme et al. (1984).

The photoluminescence spectra for two high purity MOCVD samples are shown in Fig. 2. Both of these samples were grown with TMIn metalorganic sources, but in different reactors. In sample 3, the acceptors Zn and A<sub>1</sub> are present in comparable concentrations, while Zn is the only acceptor species present in Sample 4. Comparison with the spectra in Fig. 1 from Skromme, et al., (1984) shows that the C (e - A<sup>°</sup>) transitions occur at a higher energy than the A<sub>1</sub> (D<sup>°</sup> - A<sup>°</sup>) transitions and the C (D<sup>°</sup> - A<sup>°</sup>) transitions occur at an energy between that for the Zn (D<sup>°</sup> - A<sup>°</sup>) and A<sub>1</sub> (D<sup>°</sup> - A<sup>°</sup>) transitions. Thus, it is clear that C acceptors are not detected in these MOCVD InP samples.

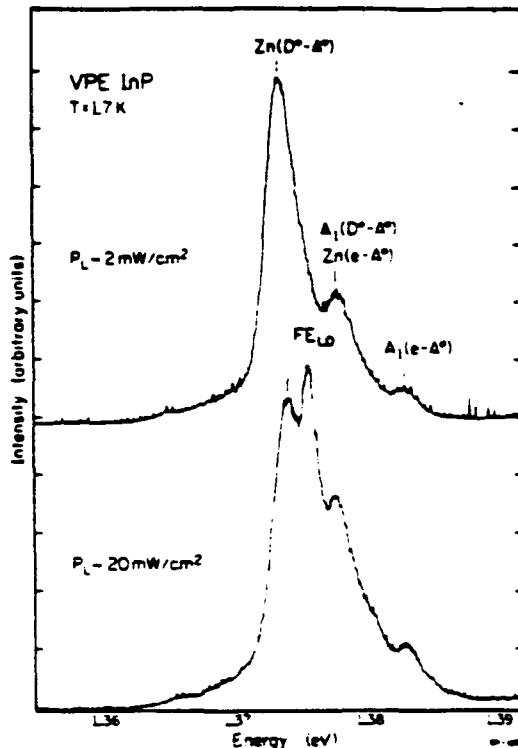
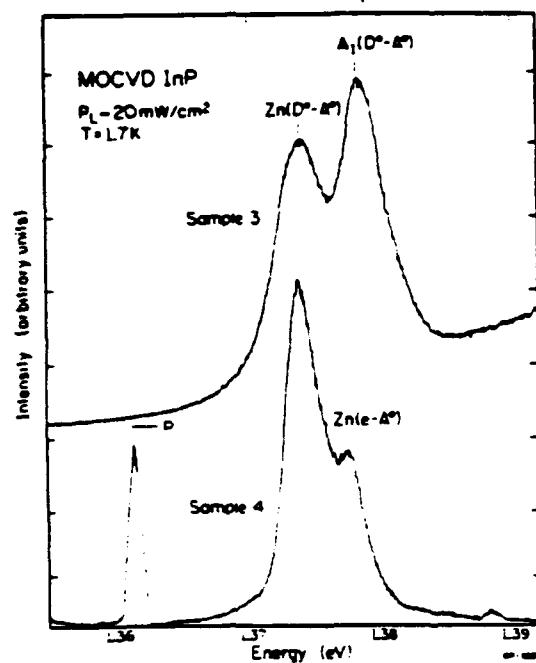


Fig. 2 PL spectra of donor-acceptor and band-acceptor transitions for two high purity MOCVD InP samples grown in different reactors. The carrier concentration and mobility at 77 K for samples 3 and 4 are  $1.2 \times 10^{15} \text{ cm}^{-3}$ , 75,000  $\text{cm}^2/\text{V}\cdot\text{s}$  and  $1.1 \times 10^{14} \text{ cm}^{-3}$ , 79,300  $\text{cm}^2/\text{V}\cdot\text{s}$ , respectively, from Skromme et al., (1984).

Fig. 3 PL spectra of donor-acceptor and band-acceptor transitions for a high purity VPE InP sample at two different excitation intensities. The  $FE_{LO}$  peak, which occurs at the same energy as the C (D<sup>°</sup>-A<sup>°</sup>) transition, becomes dominant at high excitation.

A possible complication in the PL identification of C acceptors in InP is illustrated in Fig. 3, which shows acceptor related PL spectra for a hydride VPE InP sample at two different excitation intensities. Under high excitation at low temperature, the near bandedge FE transitions in this sample become intense, and a replica of the FE transitions shifted by the LO phonon energy occurs at nearly the same energy as the C (D<sup>°</sup>-A<sup>°</sup>) transition (Bose, et al. 1989). Unless care is exercised both in the selection of the excitation conditions used for the experimental PL measurements and in the analysis of the PL data, incorrect identification of the  $FE_{LO}$  peak as C (D<sup>°</sup>-A<sup>°</sup>) transitions can result.

### 3. INTENTIONAL C DOPING WITH $\text{CCl}_4$ IN MOCVD GROWTH

Because of the desirability of a p-type dopant with low diffusion coefficient for GaAs and AlGaAs heterostructure devices, intentional carbon doping of low pressure MOCVD GaAs using a gaseous mixture of  $\text{CCl}_4$  in  $\text{H}_2$  has been studied by Cunningham, et al. (1989). Heavy carbon doping of LP-MOCVD GaAs has been obtained with a 500 ppm mixture of  $\text{CCl}_4$  in high purity  $\text{H}_2$ . With this doping source, p-type carrier concentrations as high as  $1 \times 10^{19} \text{ cm}^{-3}$  have been obtained in GaAs using trimethylgallium and arsine as the growth precursors (Cunningham, et al. 1989). The MOCVD reactor used for the growth of both the GaAs and InP in this work was an Emcore GS3100. The reactor chamber is constructed of stainless steel, with copper gaskets or Viton o-rings used for all seals. All growths were carried out on GaAs or InP substrates oriented 2° off (100) with a substrate rotation speed of

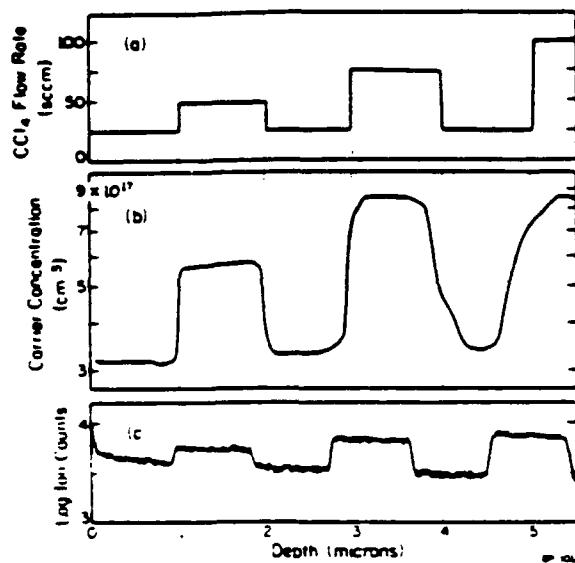


Fig. 4 Alternate lightly and heavily p-type carbon doped GaAs layers, grown with the  $\text{CCl}_4$  flow rate shown in (a). The polaron electrochemical capacitance-voltage profile in (b) shows the variation in carrier concentration with the  $\text{CCl}_4$  flow rate in this sample. The SIMS profile of the  $^{12}\text{C}$  signal as a function of depth in (c) verifies that carbon is the acceptor species.

1500 rpm. The reactor pressure was 100 Torr and a total  $\text{H}_2$  flow of 9 liters per minute was used. With the addition of  $\text{CCl}_4$ , a large increase in carbon incorporation in the epitaxial GaAs has been observed. The amount of carbon incorporated varies nearly linearly with the  $\text{CCl}_4$

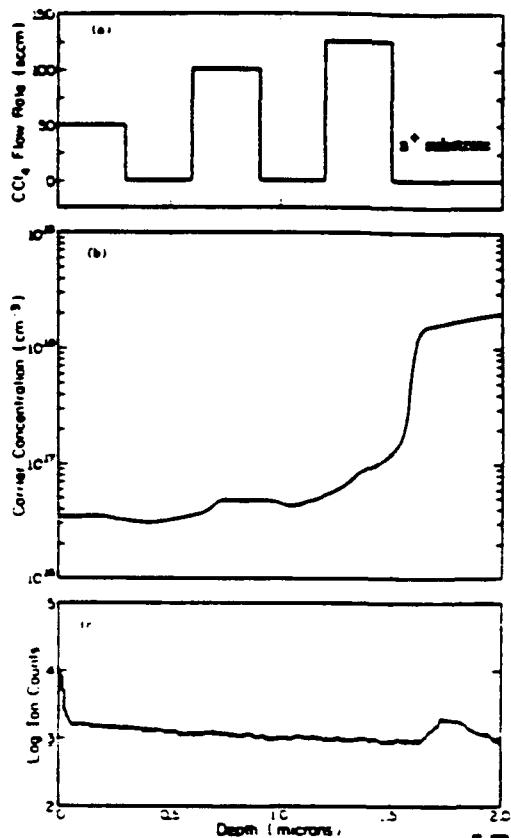


Fig. 5 The polaron electron concentration profile and  $^{12}\text{C}$  SIMS profile for an InP sample grown with the  $\text{CCl}_4$  flow rate variation shown in (a). The n-type carrier concentration as a function of depth is shown in (b). The SIMS profile of the  $^{12}\text{C}$  signal as a function of depth in (c) shows no measurable variation in the carbon concentration in this sample.

mixture flow rate. When a 1500 ppm mixture of  $\text{CCl}_4$  in  $\text{H}_2$  was used, C acceptor concentrations as high as  $4 \times 10^{19} \text{ cm}^{-3}$  were obtained.

The variation in C concentration was observed by measuring the variation in hole concentration by polaron electrochemical capacitance-voltage profiling, and by measuring the variation in the level of  $^{12}\text{C}$  by secondary ion mass spectroscopy (SIMS). Fig 4(a) shows the variation of the  $\text{CCl}_4$  flow rate during a GaAs growth at a growth temperature of  $640^\circ\text{C}$ , and a growth rate of  $1000\text{\AA/m}$ . Trimethylgallium and 100%  $\text{AsH}_3$  were the respective group III and V sources. Undoped GaAs samples grown under the same growth conditions had n-type background carrier concentrations of  $1 \times 10^{15} \text{ cm}^{-3}$ . The polaron profile of this series of layers, shown in Fig. 4(b), demonstrates that the  $\text{CCl}_4$  flow rate variation of Fig. 4(a) results in successively more heavily doped p-type layers between more lightly doped p-type layers. In order to verify that carbon is indeed the acceptor impurity, SIMS was used to measure the carbon concentration as a function of depth in this sample. The SIMS analysis for carbon was performed with a Cameca IMS-3f instrument using a  $160 \text{ nA Cs}^+$  primary ion beam at  $13 \text{ keV}$  and negative ion detection to obtain maximum carbon atom yield and detection sensitivity. Low resolution operation of this instrument results in a detection limit for  $^{12}\text{C}$  of approximately  $3 \times 10^{16} \text{ cm}^{-3}$ , below which no variation in the carbon concentration can be measured (Lum, et al. 1988), (Homma, et al. 1985). The detection limit for this instrument degrades when it is operated in the high resolution mode (Lum, et al. 1988). The SIMS profile of Fig. 4(c) demonstrates that the carbon concentration variation, and thus the hole concentration variation, results from the  $\text{CCl}_4$  flow rate variation.

In order to further study whether carbon may be incorporated into InP through intentional doping during LP-MOCVD growth,  $\text{CCl}_4$  has been added to the reactor under growth conditions similar to those used to obtain heavy carbon incorporation in GaAs. In a single InP growth run, the  $\text{CCl}_4$  flow rate was varied as shown in Fig. 5 (a), while all other growth parameters were held constant as described above for GaAs. The InP growth was on a (100) oriented S-doped substrate at  $600^\circ\text{C}$  and a growth rate of  $200\text{\AA/m}$  using trimethylindium and 100%  $\text{PH}_3$  as the group III and V sources. Undoped InP layers grown under these conditions are typically n-type with a carrier concentration of  $2 \times 10^{16} \text{ cm}^{-3}$ . The morphology of doped and undoped InP layers was speckled. The polaron capacitance-voltage profile of this series of layers, shown in Fig. 5(b), demonstrates that there is very little variation in the carrier concentration as the  $\text{CCl}_4$  flow rate is varied. Although from its behavior in GaAs carbon would be expected to be an acceptor in InP, the material actually becomes slightly more n-type with the addition of  $\text{CCl}_4$ . To examine the possibility that large amounts of electrically inactive carbon might be incorporating into the grown layers, SIMS was also used to measure the variation of carbon content as a function of depth in this sample. The SIMS profile of Fig. 5(c) shows no variation in the carbon signal above the background level, except for some carbon contamination at the substrate. The carbon detected at the substrate is likely to be the result of surface preparation, as it has been detected in either doped or undoped InP samples.

#### 4. DISCUSSION

We have attempted to incorporate carbon into LP-MOCVD grown InP by using a carbon dopant source and growth conditions similar to those used to obtain very heavy carbon incorporation in GaAs. However, in this case, in contrast to GaAs growth, SIMS and polaron electrochemical capacitance-voltage profiling of the InP layers indicate that the addition of  $\text{CCl}_4$  to the growth ambient results in no measurable change in the carbon content and no significant change in the carrier concentration. These results are in agreement with PL studies of high purity InP grown by several methods in addition to LP-MOCVD, in which no residual carbon acceptors are detected. Although ion implantation studies show that carbon is an

acceptor in InP, carbon acceptors apparently are not incorporated in InP in an electrically or optically active form during bulk, or hydride or MOCVD epitaxial growth.

However, in a recent paper on metalorganic molecular beam epitaxy (CBE/MOMBE) of InP, (Benchimol, et al., 1989) it was shown that the concentration of carbon in epitaxial InP grown by this technique varied with growth temperature, and that the electron concentration in these unintentionally doped samples showed a similar variation. These data are shown in Figure 4. (The detection limit for carbon concentration in the SIMS system used for these measurements was about  $1 \times 10^{16} \text{ cm}^{-3}$ . Although the authors of this paper did not claim that C was a donor in InP as their data indicate, it is clear that the incorporation mechanism and the reason for the difference in carbon incorporation or behavior between MOCVD and CBE/MOMBE growth of InP merits further study.

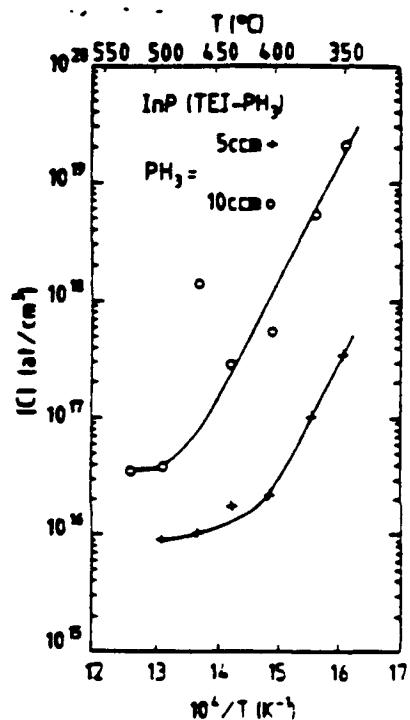


Fig. 6a Carbon concentration in InP versus inverse growth temperature for two different  $\text{PH}_3$  flow rates, 5 and 10 sccm. (From Benchimol, et al., 1989)

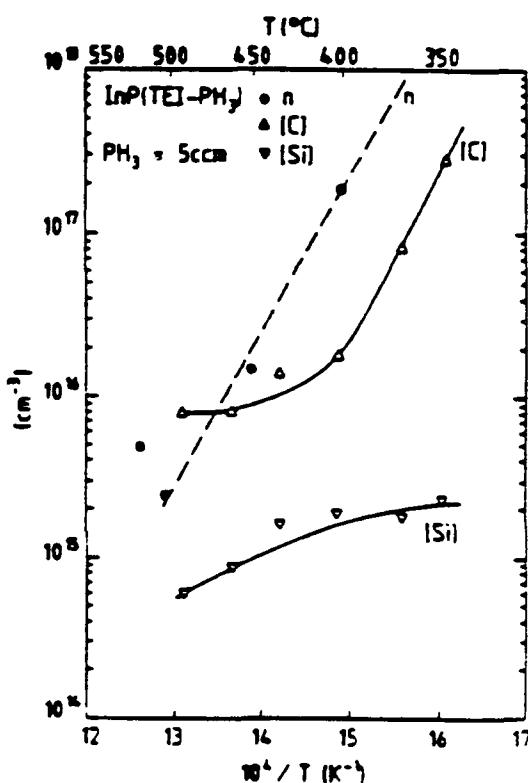


Fig. 6b Carbon [C] and silicon [Si] concentration, measured by SIMS, and net electron concentration (n), measured by Hall effect, versus inverse growth temperature, in InP grown with a  $\text{PH}_3$  flow rate of 5 sccm. (From Benchimol, et al., 1989)

The amphoteric behavior of Group IV impurities in GaAs has been the subject of considerable study. Recent results of Lee, et al. (1989 (b)) have shown that the amphoteric behavior of Group IV impurities cannot be explained by equilibrium thermodynamics alone, but that this behavior is also dependent on kinetic effects which influence impurity incorporation. It is interesting to note however, that for the case of C in LPE GaAs, the equilibrium thermodynamic model of Teamoto (1972) has been used by Low et al. (1983) to predict an

amphoteric ratio  $[C_{Ga}] / [C_{As}] = 6.4 \times 10^{-7}$  for LPE growth at 700°C, due to the large lattice strain energy contribution to the free energy difference  $\Delta G_{A/B}$  between IV<sub>Ga</sub> and IV<sub>As</sub> site occupation which forces the small C impurity onto the small As site rather than the larger Ga site. Additional contributions to the free energy difference  $\Delta G_{A/B}$  in InP due to electronegativity corrections to the band energy might preclude the incorporation of C in InP entirely at the temperatures used for MOCVD epitaxy. More experimental work remains to be done on possible orientation dependence of C incorporation in InP and in the theoretical studies of impurity incorporation in both GaAs and InP, particularly because of the recent CBE/MOMBE epitaxial results for InP.

#### ACKNOWLEDGEMENT

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## Growth on Nonplanar and Patterned Substrates

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### Extended Abstract

Organometallic chemical vapor deposition (OMCVD) has become a popular growth technique since it can be applied to the growth of the entire range of III-V compounds. In this talk, we will present our results on the growth of GaAs and InP based materials on nonplanar substrates.

The different growth rates observed on the various orientations present, when growing on a non planar substrate, can be used to obtain lateral patterning of thickness. The lateral variations in thickness translate into lateral variations in the effective bandgap when quantum wells are grown on non planar substrates. Therefore, carriers can be confined both in the growth direction and laterally by growing quantum well heterostructures on non planar substrates. If the lateral confinement occurs over sufficiently small dimensions, quantum wire and box structures can be achieved. In this talk we show how quantum wire GaAs/AlGaAs laser structures were achieved by OMCVD growth on non planar GaAs substrates. The growth features obtained are compared to those obtained in MBE and OMMBE growth and shown to be due to a combination of gas phase and surface diffusion.

Growth on non planar substrates can also be used to fabricate waveguides. By making use of the {111}B non growth facet that develops when growing on [011] oriented mesas, rib waveguides with walls that are smoother than that can be obtained by etching can be grown. Waveguides with losses less than 0.6 dB/cm at 1.52  $\mu$ m have been obtained by this technique. Varying the width of the mesas across the wafer causes the thickness of the layers growing on top of the mesas to vary. This can be used to fabricate tapered waveguides.

Growth on vicinal (100) GaAs substrates with grooves etched in them result in the formation of macro-steps. Such steps can be used to fabricate a lateral and vertical array of quantum wires.

By growth on partially masked substrates we demonstrate that lateral thickness patterning can also be achieved. These experiments also show the importance of gas phase diffusion in determining the growth behaviour.

Growth of InP based materials on non planar substrates is more difficult than that of GaAs based materials due to the problem of lattice mismatch that can occur. However, by a careful choice of crystallographic planes on which growth occurs this problem may be overcome.

The orientation dependence of doping can be used to obtain lateral patterning of doping by growth on non planar substrates. By this technique device fabrication may be simplified and novel devices may be grown. We show how lasers with current confinement layers may be grown in a single growth step instead of three.

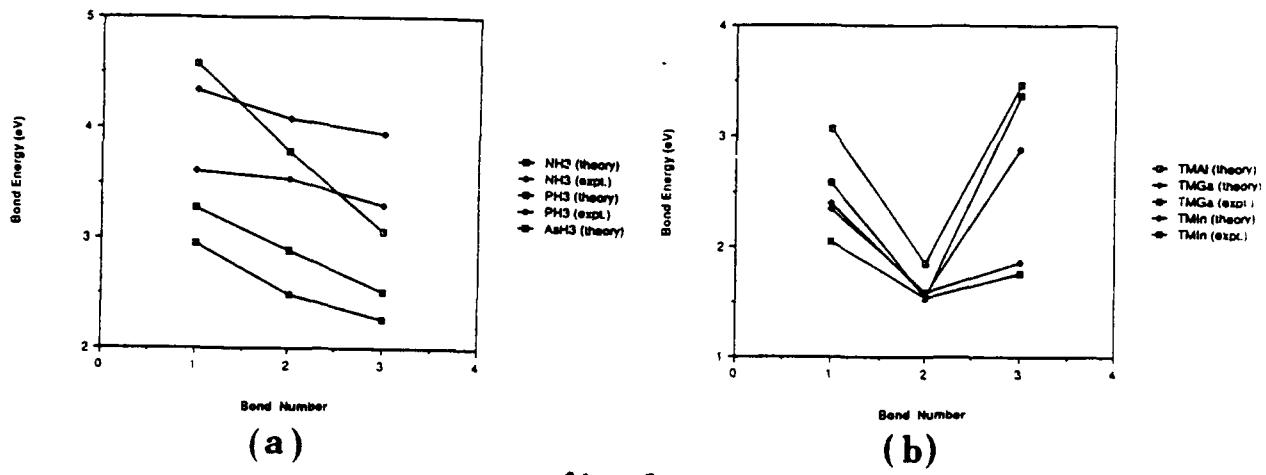


fig. 1

Table I: Equilibrium geometries and X-Y bond strengths for  $(CH_3)XYH_3$  adducts. Here, X = Al, Ga, and Y = N, P, As. R(eq.) refers to the X-Y bond in Angstroms. Angles are in degrees.

X	Y	R(eq.)	$\angle X-Y-H$	$\angle Y-X-C$	D(X--Y)
Al	N	2.15	109.42	99.3	1.13 eV
Al	P	2.83	119.42	96.13	0.33 eV
Ga	N	2.23	108.9	98.4	0.88 eV
Ga	P	2.97	119.05	94.83	0.25 eV
Ga	As	---	Not Bound!		

Table II. Bond strengths for Ga-N adducts with different ligand arrangements.

Molecule	Bond strength (eV)
$(CH_3)_3GaNH_3$	0.88
$GaN(CH_3)_6$	1.02
$GaNH_6$	1.25
$H_3GaN(CH_3)_6$	1.72

Might expect a different ordering for heavier group atoms

# Growth of High Quality AlGaAs by MOMBE Using Trimethylamine Alane

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## ABSTRACT

AlGaAs grown by MOMBE has been problematic due to oxygen and carbon contamination, particularly when triethylaluminum (TEAl) has been used as the aluminum source. Consequently, we have investigated trimethylamine alane ( $\text{TMN} \cdot \text{AlH}_3$ ) as a potential replacement for the conventional metal-organic Al sources. AlGaAs films with excellent structural and optical properties have been grown with this source. Photoluminescence intensities from AlGaAs grown by MOMBE at 500°C using  $\text{TMN} \cdot \text{AlH}_3$  are comparable to those from material grown by metalorganic chemical vapor deposition at 675°C using trimethylaluminum (TMAI). Carbon and oxygen levels in MOMBE grown AlGaAs are drastically reduced in comparison to similar films grown with TEAl.

Metal Organic Molecular Beam Epitaxy (MOMBE) is considered a potential universal epitaxial growth technique for III-V heterostructures, with the capability to prepare any combination of In, Ga, Al, As, P or Sb with dimensional and compositional control comparable to elemental source MBE. Although the same III-V elements can be incorporated in epitaxial layers by MOCVD, in practice attaining precise control of the growth parameters is difficult because of the complex gas flow dynamics. Alternatively, the universality of MBE is compromised by its inability to grow P-containing films in a reproducible manner due to the allotropic nature of phosphorus.

MOMBE using group III alkyls together with  $\text{AsH}_3$  and  $\text{PH}_3$  has been successfully applied to the growth of high quality GaAs, InP and InGaAs films. In contrast, the preparation of AlGaAs by MOMBE has proven difficult. Our initial experiments employing elemental As, triethylgallium (TEGA) and triethylaluminum (TEAl) resulted in unsatisfactory morphology and marginal single crystallinity as determined by ion channeling. Replacing As with  $\text{AsH}_3$  produced a marked improvement in both morphology and crystalline quality. Under the best conditions, however, the oxygen level greatly exceeded  $10^{19}\text{cm}^{-3}$ , precluding n-type doping. An additional concern with the use of TEAl is carbon contamination resulting from the strength of the Al-C bond in this chemical. The high oxygen concentration can be readily understood in light of the oxygen affinity of TEAl which forms volatile alkoxides [e.g.  $(\text{C}_2\text{H}_5)_2\text{AlOC}_2\text{H}_5$ ] with vapor pressure comparable to the precursor itself. Oxygen may enter the TEAl bubbler via small leaks and backstreaming, or it may be present in the as-received bubbler. The purity of TEAl appears to be supplier and batch dependent.

Some limited success in using TEAl to grow AlGaAs by MOMBE has been reported. Hwang et al.<sup>1,2</sup> grew High Electron Mobility Transistor (HEMT) structures with a  $77_{\text{eK}}$  mobility of  $47,000 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$  for a  $30\text{\AA}$  spacer. However, the C contamination in  $\text{Al}_3\text{Ga}_7\text{As}$  was high ( $\sim 10^{17}\text{cm}^{-3}$ ), and the hole concentration in undoped AlGaAs was

extremely sensitive to Al concentration and growth temperature. Ando et al.<sup>3</sup> reported oxygen levels in excess of  $3 \times 10^{17} \text{ cm}^{-3}$  that increased by two orders of magnitude when elemental As replaced AsH<sub>3</sub>. The carbon content ranged from  $10^{18}-10^{19} \text{ cm}^{-3}$ .

Obviously there is a need for an alternative robust and reproducible MO-Al source for MOMBE. Tri-isobutyl aluminum (TiBAI) has been employed but is of limited use in view of its low vapor pressure and instability.<sup>4</sup> We demonstrate MOMBE growth of superior quality Al<sub>x</sub>Ga<sub>1-x</sub>As using trimethylamine alane (TMN · AlH<sub>3</sub>). This precursor contains no direct Al-C bonds and the oxygen contamination is vastly suppressed by the formation of the less volatile Al-OH species rather than the alkoxide. The resulting AlGaAs is of comparable quality to the best MOCVD material in terms of luminescent intensity.

AlGaAs layers were grown on 2"  $\phi$  GaAs wafers in a Varian Gas Source Modular Gen II. GaAs buffer layers of 1000Å were grown prior to deposition of the AlGaAs, and 50Å GaAs cap layers were grown on top of the AlGaAs. TEGa, TEAl, and TMN · AlH<sub>3</sub> were transported into the chamber via a hydrogen carrier gas. Growth conditions, Al source carrier gas flow rate, and AsH<sub>3</sub> flow were held constant for all of the growth runs. The TMN · AlH<sub>3</sub> bubbler temperature was set at 4°C so that the growth rate of AlAs at 500°C was the same for either TEAl or TMN · AlH<sub>3</sub>. Al mole fraction was varied by changing the flux of TEGa. Growth experiments involving TEAl were conducted first. The alkyl module was then thoroughly purged and the TEAl source was replaced with the TMN · AlH<sub>3</sub> bubbler.

The AsH<sub>3</sub> was cracked in a Varian low pressure cracker set at a temperature of 950°C. The growth temperature was 500°C as measured by the substrate thermocouple. Previous calibrations with an optical pyrometer and observation of the InSb melting point indicate that the actual surface temperature is ~480°C. The growth rate was 0.5 – 1.3  $\mu\text{m}/\text{hr}$ . for the AlGaAs and 1.2  $\mu\text{m}/\text{hr}$ . for the GaAs.

The morphology of layers grown with TMN · AlH<sub>3</sub> is featureless, as can be seen in Fig. 1. Further evidence of the excellent crystallinity has been seen with RBS which shows a  $\chi_{\min}$  of 4% for Al<sub>57</sub>Ga<sub>43</sub>As grown from TEGa and TMN · AlH<sub>3</sub>. In contrast, Al<sub>53</sub>Ga<sub>47</sub>As grown under identical conditions using TEAl shows a  $\chi_{\min}$  of 23%.

Using TEAl, we have explored a wide range of growth conditions and have been unable to produce luminescent material under any conditions. With TMN · AlH<sub>3</sub>, however, we have been able to grow luminescent material quite easily. Fig. 2 shows the room temperature PL spectra of an undoped Al<sub>23</sub>Ga<sub>77</sub>As layer grown with TMN · AlH<sub>3</sub>. In contrast to material grown with TEAl, these samples exhibit very strong luminescence. For comparison a room temperature PL spectra from material grown by MOCVD at a substrate temp of 675°C is also given in Fig. 2. The AlGaAs grown by MOMBE shows similar PL intensity to that grown by MOCVD, in spite of the very low growth temperature. Typically luminescence intensity falls off with growth temperature. With TMN · AlH<sub>3</sub>, however, material with good optical quality can be produced even at low growth temperatures. We are also able to achieve n-type doping of the AlGaAs, which could not be done when using TEAl.  
*in our n;34th*

The optical quality of the material is directly related to the oxygen content of the film. SIMS analysis of Al<sub>53</sub>Ga<sub>47</sub>As grown from TEAl, Fig. 3, shows a very high oxygen contamination level of  $10^{21} \text{ cm}^{-3}$ . It is quite possible that this source was contaminated due to the failure of a component in the gas manifold. However, it serves to demonstrate the sensitivity of TEAl to oxygen contamination. This sensitivity places great demands both on the equipment and on the supply process for the metal-organic source. Therefore it is clear that a more robust source is needed.

In contrast, Al<sub>57</sub>Ga<sub>43</sub>As grown from TMN · AlH<sub>3</sub> shows a much lower oxygen level of  $\sim 2 \times 10^{18} \text{ cm}^{-3}$ , Fig. 3. Thus, without altering the gas handling or growth system in any way,

the oxygen level has been reduced almost three orders of magnitude.

*Start In MOCVD  
first Al<sub>3</sub>*

In addition to oxygen contamination, unintentional carbon incorporation has also been a problem for AlGaAs grown by MOCVD. For the samples examined in this study, carbon levels in Al<sub>53</sub>Ga<sub>42</sub>As layers grown from TEAl are  $3 \times 10^{18} \text{ cm}^{-3}$ , Fig. 3. Though it is possible to reduce this level to  $\sim 1 \times 10^{18}$  by altering the growth conditions, the carbon background is still higher than what can be achieved by other growth techniques. In contrast, similar layers grown from TMN · AlH<sub>3</sub> show a carbon level which is at or below the detection limit of SIMS,  $\sim 2 - 3 \times 10^{17} \text{ cm}^{-3}$ .

If this reduction in carbon were due only to the absence of an Al-C bond in the source compound, one would expect the use of elemental Al to produce low carbon material as well. This is not the case, however. Al<sub>36</sub>Ga<sub>64</sub>As grown with elemental Al and As and TEG shows a background doping of  $8.4 \times 10^{16} \text{ cm}^{-3}$  as determined from Hall measurements. It appears that carbon, in the form of ethyl or methyl radicals, is being transferred from the adsorbed TEGa, or DEGa, to the adsorbed Al. Since the Al-C bond is quite strong, this species does not decompose as readily as the Ga-C species. Thus, the carbon concentration is much higher in AlGaAs grown from elemental Al than one would expect based on the background doping of GaAs grown under similar conditions where  $p \leq 10^{15} \text{ cm}^{-3}$ .

One obvious approach to this problem is to enhance the formation of ethane by flooding the surface with excess hydrogen. We have found that the introduction of diatomic hydrogen does not significantly affect the growth chemistry; therefore, atomic hydrogen is required. While in principle this approach is straightforward, the generation of atomic hydrogen in the growth chamber could lead to technical problems, such as furnace failure at high temperatures in the presence of alkyls.

The most desirable solution is a source, either Group III or Group V, which can transport hydrogen to the wafer surface and then decompose leaving atomic hydrogen at the growth

interface. This hydrogen would then retard the transfer of hydrocarbon species to the Al. AsH<sub>3</sub> can produce this effect to a limited degree. In fact, without AsH<sub>3</sub>, i.e. using elemental As, we have found that AlGaAs grown from TEAl and TEGa is of very poor structural quality. Due to safety considerations and the poor cracking efficiency of this gas in UHV conditions, the amount of atomic hydrogen which can be produced from this source is a small fraction of the total flux.

TMN · AlH<sub>3</sub>, however, is a good candidate for atomic hydrogen transport. Given the low decomposition temperature of this source, ~90°C at atmospheric pressure, one would expect the trimethylamine adduct to break from the alane quite easily on the wafer surface. We have seen no evidence in the growth chamber mass spectrometer to dispute this. Once the adduct is removed, the alane molecule, which is highly unstable, then decomposes on the surface or reacts with other surface species. If the molecule decomposes, leaving Al and atomic hydrogen, the hydrogen would then react with adsorbed ethyl radicals from the TEGa forming ethane rather than Et-Al or Me-Al. It is also possible that the alane reacts with the adsorbed TEGa, or DEGa, and forms ethane directly. In either case, the net result would be a significant reduction in the carbon concentration. The low background levels observed in the grown layers suggests that TMN · AlH<sub>3</sub> is indeed providing atomic hydrogen to the growth surface. It is quite possible, in fact, that the removal of the carbon by the alane is so efficient that high quality material could be grown using elemental As rather than AsH<sub>3</sub>.

In conclusion, we have obtained MOMB E grown AlGaAs with excellent optical and structural quality through the use of TMN · AlH<sub>3</sub> instead of the conventional TEAl source. Though some areas require further investigation, such as source stability, the preliminary results are quite encouraging and suggest that it may be possible to grow high quality device structures at relatively low temperatures.

*Acknowledgements*

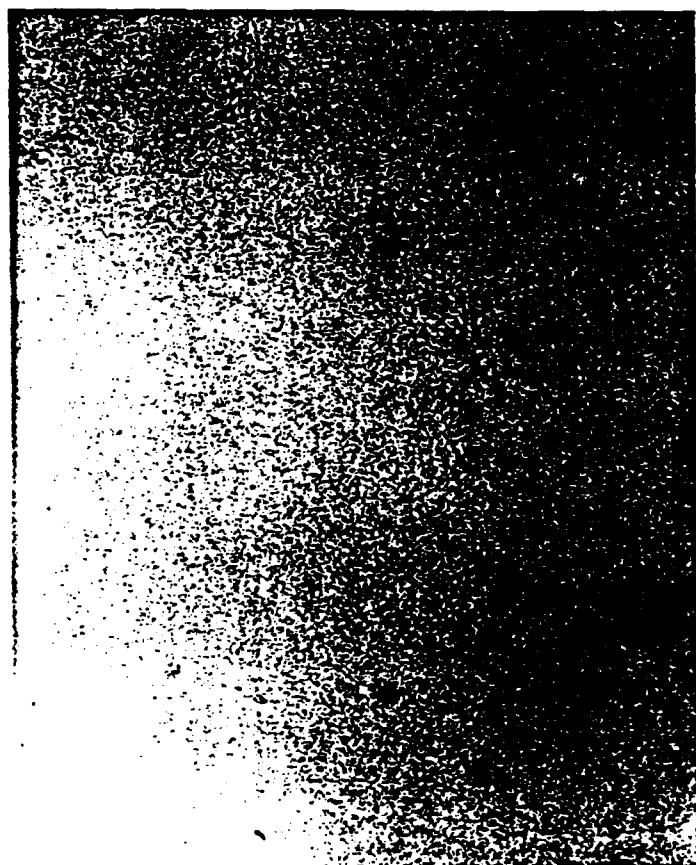
We are grateful to Dr. A. Robertson for useful discussions of MOMBE surface chemistry and thank A. P. Kinsella for the photoluminescence measurements. The continuing interest of Dr. S. S. Pei is greatly appreciated. This work was partially supported by the Materials Laboratory, WRADC under US Air Force Contract No. F33615-87-C-5244.

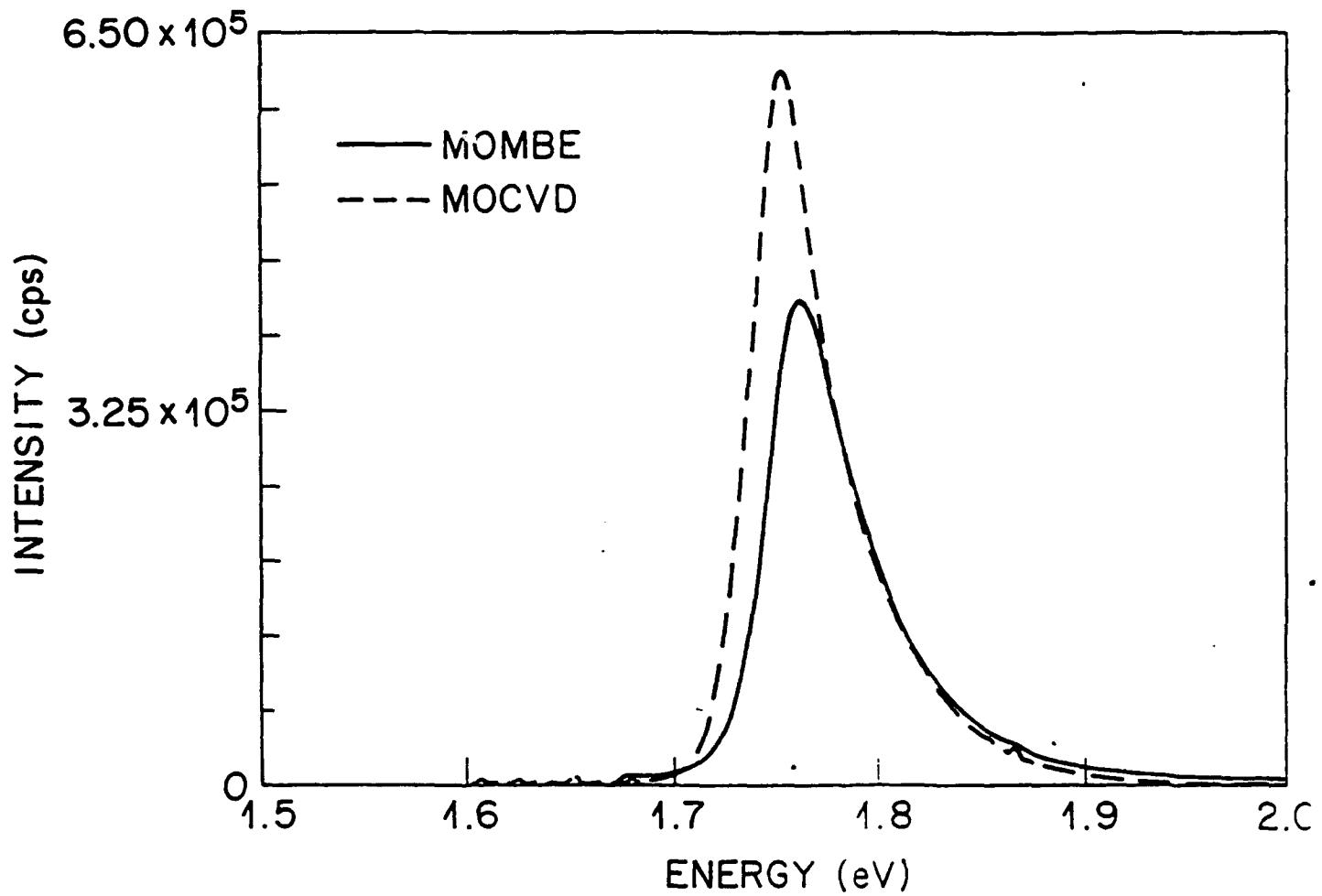
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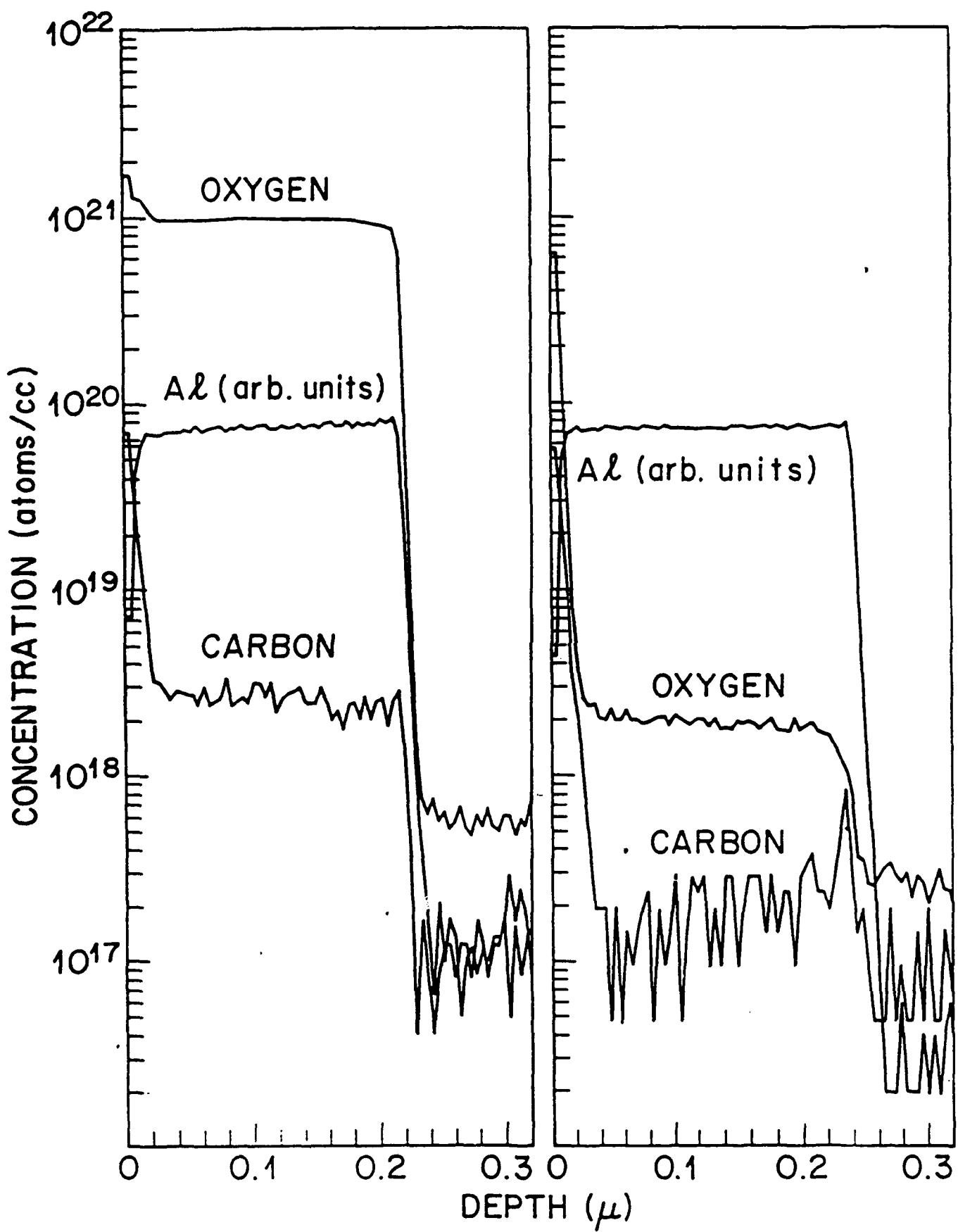
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### Figure Captions

- Fig. 1** Nomarski photograph of  $\text{Al}_{57}\text{Ga}_{43}\text{As}$  layer grown using  $\text{TMN} \cdot \text{AlH}_3$  (1000X).
- Fig. 2** Room temperature PL spectra from AlGaAs grown at  $675^\circ\text{C}$  by MOCVD and at  $500^\circ\text{C}$  by MOMBE using  $\text{TMN} \cdot \text{AlH}_3$ .
- Fig. 3** SIMS atomic profiles of C and O in  $0.2 \mu\text{m}$  thick AlGaAs layers grown on GaAs buffers using either TEAl as the source chemical for Al (at left) or using  $\text{TMN} \cdot \text{AlH}_3$  (at right).







## Optical Approaches to Real-Time Analysis and Control of Semiconductor Crystal Growth

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A variety of optical methods are now being developed to study surface processes and to monitor and control layer thicknesses and compositions during semiconductor crystal growth by molecular beam epitaxy (MBE), organometallic chemical vapor deposition (OMCVD), organometallic molecular beam epitaxy (OMMBE), and related techniques. Spectroellipsometry (SE) and spectroreflectometry (SR), the older, primarily bulk-sensitive optical probes, are now augmented by new, primarily surface-sensitive probes such as reflectance-difference spectroscopy (RDS), second-harmonic generation (SHG), and laser light scattering (LLS). A recent review is available.<sup>1</sup>

Here, I summarize results obtained with two approaches: RDS, a normal-incidence optical technique that takes advantage of symmetry to suppress the dominant (~99%) bulk contribution to the overall optical signal and enhance the ordinarily weak surface contribution,<sup>2</sup> and SE, which returns information integrated over the entire penetration depth of light.<sup>3</sup> The two approaches are complementary. RDS allows us to obtain information about growth surfaces, which is needed to address the scientific problem of the physics and chemistry of semiconductor crystal growth. SE allows us to obtain information about layer thicknesses and compositions, which is needed to address the technological problem of monitoring and controlling growth.

RDS has now demonstrated the capability not only of following growth kinetics,<sup>4,5</sup> but also of determining surface dielectric responses directly.<sup>6</sup> The first application of RDS to crystal growth was to follow changes in surface chemistry and structure on (001) GaAs during crystal growth by MBE as the fluences of Ga and As impinging on the growth surface were changed.<sup>4</sup> These changes showed a strong spectral dependence, which was recently interpreted by theoretical calculations<sup>6,7</sup> as involving transitions between Ga dimer bonds and empty Ga dangling orbitals and between As lone-pair orbitals and empty As dimer antibonding levels. In applications to OMCVD, the time, temperature, and pressure dependences of the RD response of (001) GaAs growth surfaces established that OMCVD growth rates under atmospheric-pressure conditions from trimethylgallium and arsine sources were determined by a competition between desorption and decomposition of TMG chemisorbed via an excluded-volume mechanism.<sup>5,8</sup>

Although ellipsometry was first used about 10 years ago to monitor semiconductor crystal growth,<sup>9</sup> the work was not followed up owing to sensitivity problems and difficulties encountered in the early stages of OMCVD growth technology.

Recently, SE has been applied to monitor growth of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  by OMMBE.<sup>10</sup> Although the recent work was also done at a single wavelength, the use of a spectroscopic instrument allowed this wavelength to be chosen so as to optimize sensitivity to alloy composition in the near-surface region. These results indicated that  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  compositions of 10 Å films could be determined to a precision of 3% with corresponding tradeoffs in sensitivity for thinner or thicker films. More recently, compositional information provided by ellipsometric measurements were used to control the flow of triethylaluminum to the OMMBE growth chamber and therefore the composition  $x$ , thus realizing the first closed-loop noninvasive optical system actually to control crystal growth.<sup>11</sup>

The rapid development of optical techniques is providing new opportunities for fundamental and applied studies of semiconductor crystal growth, a field formerly off-limits owing to the hostile environments in which crystal growth occurs.

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# **PHOTOREFLECTANCE FOR IN-SITU MONITORING OF THIN FILM**

**GROWTH\***

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**Photoreflectance (PR), a contactless form of modulation spectroscopy, is a powerful tool for the in-situ monitoring/control of the growth of thin film semiconductors .Photoreflectance is non-invasive, requires no special mounting of the sample and can be employed in any transparent medium and there is no need for cryogenic temperatures. The apparatus is relatively simple, inexpensive ,easy to use and compact. Topographical scans can be performed.A great deal of information can be obtained per dollar of investment.**

**Modulation spectroscopy involves a very general principle of experimental physics. Instead of detecting the absolute optical spectrum, measure the derivative with respect to some modulating parameter. In PR the built-in electric field is modulated by means of photo-injected electron-hole pairs created by a chopped pump beam.**

**Photoreflectance yields sharp, derivative-like spectra in the region of interband transitions whose lineshape can easily be fit to yield band gap energies and broadening parameters. Even at 300K it is possible to determine energy gaps to within a few milli-electron volts.**

**This talk will discuss recent experiments using PR to measure the direct band gaps ( $E_0$ ) of GaAs, InP, GaAlAs and InGaAs (  $x = 0.07$  and  $0.16$  ) to over  $600^{\circ}\text{C}$  under actual growth conditions including rotating substrates (500 rev/min). For these semiconductors  $E_0$  can be evaluated to  $\pm 5$  meV at these elevated temperatures. Thus the temperature of GaAs and InP substrates could be determined to**

**$\pm 10^{\circ}\text{C}$ . Also the Al composition of GaAlAs and In content of InGaAs could be monitored during actual growth. Topographical scans can be performed. Measurements can be made at present in about 30 seconds and 15 seconds seems feasible. Thus PR could be used for monitoring/control of actual growth parameters such as substrate temperatures and alloy composition.**

**\*Work performed in collaboration with Z. Hang of Brooklyn College and H. Shen of GEO-CENTER, Inc., Ft. Monmouth, NJ 07703**

## **GROWTH AND DOPING MECHANISMS FOR HgCdTe\***

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Today, a major program is being undertaken with the goal of fabricating large area focal plane arrays using HgCdTe. Models for the growth and doping of this semiconductor are of critical importance if this goal is to be met. The starting point for developing these models is a study of the growth and doping of CdTe. To do so, a series of experiments have been conducted, as follows [1]:

The decomposition of dimethylcadmium (DMCd) was studied by observing the growth of Cd on a cold ( $< 150^{\circ}\text{C}$ ) substrate, in a reactor whose wall was kept hot, in the  $230\text{-}400^{\circ}\text{C}$  range. Here, an activation energy of 20.8 kcal/mole was measured. In contrast, experiments with the decomposition of CdTe on a hot susceptor, with a cold wall, resulted in no deposit, even when the partial pressure of DMCd was 50 times higher than the equilibrium vapor pressure of Cd over Cd. Together, these experiments lead to the conclusion that the decomposition of DMCd is surface catalyzed and results in the adsorption of Cd on the substrate.

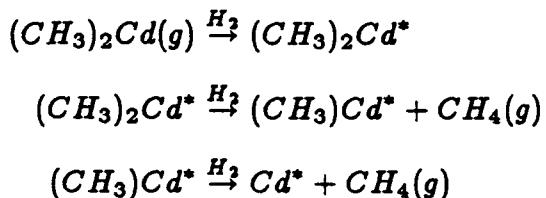
The results of experiments with the growth of CdTe from DMCd and diethylteluride (DETe) show an activation energy of about 22 kcal/mole for growth on (100) CdTe, (1000)  $\text{Al}_2\text{O}_3$ , (100) GaAs, and (100) InSb.

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\*Work done in collaboration with I.B. Bhat, P. Agnello, P. Chinoy, H. Ehsani, K. Parat, N. Taskar.

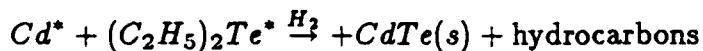
In yet another experiment, we have shown that CdTe can be grown on a variety of substrates, using Cd vapor and DETe, at temperatures as low as 230°C where DETe is found to be very stable. This experiment shows that it is not necessary to evoke the formation of an adduct of DMCd and DETe to explain the growth of CdTe. This does not, however, preclude the possibility of adduct formation in the gas phase.

Based on the above, we propose that CdTe deposition occurs by the following mechanisms



where \* represents absorbed molecules.

In the absence of any DETe, the decomposed Cd may leave the surface, because no overpressure of Cd is present to prevent its evaporation in a flowing open-tube system. If DETe is present, however, it can be physisorbed, accompanied by surface diffusion. Now, the decomposition of DETe can be enhanced by the presence of Cd\* as follows



The above reaction is probable because the establishment of the Cd-Te bond can facilitate the breaking of the Te-ethyl bond of DETe molecules absorbed on or near cadmium. This is very well supported by our results that CdTe growth is possible using elemental Cd and DETe at 230°C. The vapor pressure of both of the elements over CdTe is low (less than  $10^{-8}$  torr at 350° over CdTe), so that evaporation of CdTe is not expected. However, the growth rate is limited by kinetic processes.

P-type doping of CdTe has generally been considered to be difficult to achieve. In part, this is because the preferred Column III dopants behave as singly ionized acceptors if they substitute on Te-sites, but as triply ionized donors on Cd-sites. Often, doping with Column III elements results in n-type behavior and in highly compensated material.

In our experiments, we attempted, without success, to dope CdTe by means of an elemental arsenic source. On the other hand, the use of arsine gas was very successful [2] and resulted in hole concentrations as high as  $3 \times 10^{17}/\text{cm}^3$ . Large area samples (1.5 cm  $\times$  1.5 cm) were doped in this manner, without recourse to laser stimulation which is necessary for p-doping in MBE.

A tentative model can be proposed to explain the success of p-doping of CdTe with arsine gas. DMCd is adsorbed as Cd\* on the growing surface. Simultaneously, AsH<sub>3</sub> is co-adsorbed as As-H on the CdTe surface, following the lines of the model we have proposed for the growth of GaAs [3]. Alternatively, it is possible that the adsorbed species is an adduct. Finally, reaction of Cd\* and As-H results in the simultaneous incorporation of Cd on Cd-sites, with As as its nearest neighbor, i.e., on Te-sites. This would lead to p-CdTe with low compensation. Hall measurements on p-CdTe doped by this technique have resulted in mobility values comparable to the best values reported for bulk CdTe, which would support the claim of low compensation.

Growth of HgCdTe has been carried out by the simultaneous pyrolysis of Hg, DMCd and DMTe. Here, we find that the growth can be modeled as the simultaneous growth of HgTe and CdTe, so that

$$R_{HgCdTe} = (K_{CdTe}\theta_{Cd} + K_{HgTe}\theta_{Hg})\theta_{Te}$$

where  $K$  represents the surface reaction rate constants and  $\theta$  are the surface coverages.

Assuming non-competitive adsorption of Te on Column VI sites and competitive

adsorption between Cd and Hg for Column II sites, we obtain

$$R_{HgCdTe} = \left( \frac{K_{CdTe}\beta_{Cd}P_{Cd} + K_{HgTe}\beta_{Hg}P_{Hg}}{1 + \beta_{Cd}P_{Cd} + \beta_{Hg}P_{Hg}} \right) \theta_{Te}$$

Similar assumptions have been made to develop models for the growth of ternary alloys such as GaAlAs. Here, the rate equations governing the growth of the separate binaries can be considered to be independent of each other. As a result, the composition is essentially determined by the gas mixing of the respective alkyls before entering the reaction chamber. This means that the composition uniformity is assured, regardless of reactor flow conditions. Figure 1a shows the basic growth characteristic of such alloys.

The growth characteristic of HgCdTe is quite different, as seen in Fig. 1b. As a result, composition uniformity of this alloy is not simply related to the inlet reactant composition.

A start towards the modeling of HgCdTe growth can be made by proposing that the adsorption rate of Hg and the coverage of Cd are related by the Elovich equation. With reasonable approximations, this states that

$$\beta_{Hg} = \beta_{oHg} e^{-E'(\theta_{Cd})}$$

where  $\beta_{oHg}$  is the value for zero Cd coverage. Our growth experiments have shown that the growth rate of the CdTe component is almost linear with  $P_{DMCd}$ . Thus, we can write

$$\beta_{Hg} \sim \beta_{oHg} e^{-E(x_{Cd}^v)}$$

where  $x_{Cd}^v = P_{DMCd}/(P_{DMCd} + P_{Hg})$ .

Substituting into the overall growth rate equation gives

$$\frac{R_{HgCdTe}}{\theta_{Te} K_{HgTe} \beta_{oHg}} = \left( \frac{K_{CdTe}}{K_{HgTe}} \right) \left( \frac{\beta_{Cd}}{\beta_{oHg}} \right) P_{Cd} + e^{-E(x_{Cd}^v)} P_{Hg}$$

Solving this equation for a different number of growth conditions leads to the following results:

1. The overall sticking coefficient of Cd\* is relatively constant with  $x_{Cd}^v$ , at a value of about  $1 \times 10^{-4}$ .
2. The overall sticking coefficient of Hg falls with increasing  $x_{Cd}^v$ , and is about 3 orders of magnitude smaller than that of Cd.
3. The adsorption/desorption rate constant ratio for Hg is given by the Elovich relation, with

$$\beta_{Hg} = \beta_{oHg} \exp[-(8.7 \times 10^2 - 1.45 \times 10^5 x_{Cd}^v) x_{Cd}^v]$$

This equation is specific to growth at one particular growth temperature, 415° in our case.

The p-doping of HgCdTe has only been recently accomplished by us [4], using arsine as the dopant source. Here, our results (see Fig. 2) show a saturation of p-doping at about  $2 \times 10^{17}/\text{cm}^3$  with mobility values comparable to those of bulk material.

Experiments on the Hg-pressure dependence of p-doping have shown a linear dependence of the hole concentration on the Hg-pressure. This fact, together with the high values of hole mobility, indicates that the layers are not compensated, and that arsenic is incorporated almost entirely on Te-sites. Moreover, the SIMS count for arsenic in these layers is linear with the hole concentration as seen in Fig. 3. This indicates that the surface coverage of arsenic (or an arsenic species) is the limiting factor in the incorporation of this dopant.

The above observations, combined with those for the doping of CdTe, lead to the following tentative model for arsenic incorporation in HgCdTe.

1. Arsine is delivered to the reactor and adsorbed on the substrate as As-H or an As-species of an adduct nature.
2. The overall sticking coefficient of this As-species is about 290 times lower than that of Cd\*. Moreover, this sticking coefficient falls with arsine overpressure. We believe that its adsorption/desorption ratio is a function of the coverage of both Hg and the arsenic species, but have insufficient data to model its behavior in a quantitative manner.
3. Arsenic incorporation comes about by the formation of Cd-As on the surface, with the As preferentially incorporated in Te-sites as part of the growing layer.
4. Arsenic incorporation in HgCdTe is limited by the surface coverage of the arsenic species, rather than by its incorporation into compensating inactive sites. As a result, the hole mobility value equals that of bulk material, even well into the saturation region.

The n-type doping of HgCdTe is relatively easy to accomplish, with Column III sources preferred because of their thermal stability. Our work has focused on indium, using trimethylindium (TMI) as the dopant source. (Some work has also been carried out with triethylindium.) Doping to  $4 \times 10^{18}/\text{cm}^3$  has been achieved, as shown in Fig. 4, with the doping concentration varying inversely with Hg partial pressure. Moreover, the mobility is comparable to that of bulk HgCdTe and MBE grown material of the same doping level. Taken together, this implies that the indium is located in Column II sites, with a low degree of compensation.

Figure 5 shows the FTIR data for two layers grown under identical conditions, with different doping levels. Commonly, this shift in the optical bandgap has been interpreted as an increase in the Cd-fraction with doping level. We have studied this effect, with a view to its implications for the incorporation model of In in HgCdTe. Our study has shown that a Burstein-Moss shift can be used to explain the results, within experimental

error. This shift is large because of the non-parabolic nature of the conduction band of HgCdTe. Edax measurements (courtesy of Dr. H.F. Schaake, Texas Instruments Co.) have shown that the actual Cd-fraction does not vary with the doping concentration, as shown for two pairs of matched samples in the attached Table.

We conclude, therefore, that the growth model for n-HgCdTe is relatively straightforward. TMI is transported to the growth substrate, where it is adsorbed as Me-In or as In\*. We have no evidence at the present time as to which of these species is involved. The doping concentration is relatively independent with composition, which leads us to conclude that the indium species coverage is not related to the Cd or Hg partial pressure, to any measurable extent.

## CONCLUSION

Tentative models have been proposed for the growth and doping of CdTe and HgCdTe. Much further work needs to be done, especially in the area of HgCdTe. This work will be necessary in order to bring the development of far infrared detectors to a commercial stage.

## ACKNOWLEDGEMENT

This work was supported by DARPA Contract No. N-00014-85-K-0151 through the Office of Naval Research, by a fellowship from the IBM Corporation and by partial funding from the Raytheon Corporation and ITT Corporation. Substrate material was kindly provided by C.J. Johnson and S. McDevitt of II-VI, Inc. This support is gratefully acknowledged.

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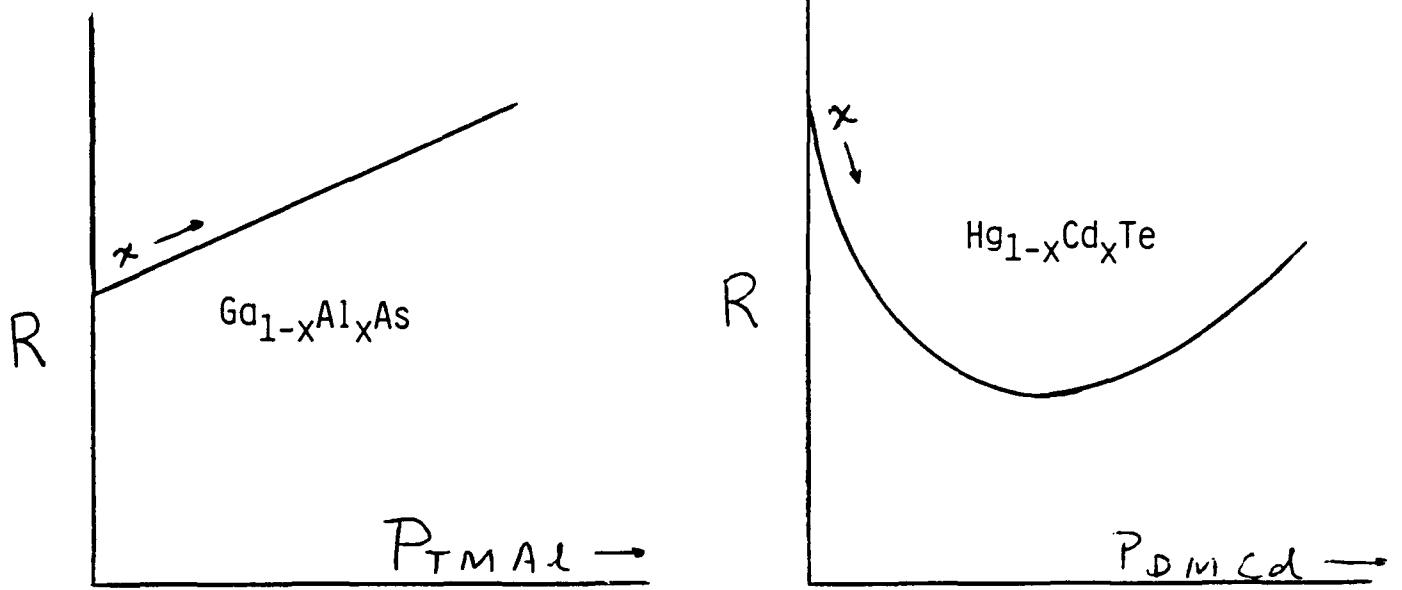


Fig. 1 (a) Growth characteristic of GaAlAs  
(b) Growth characteristic of HgCdTe

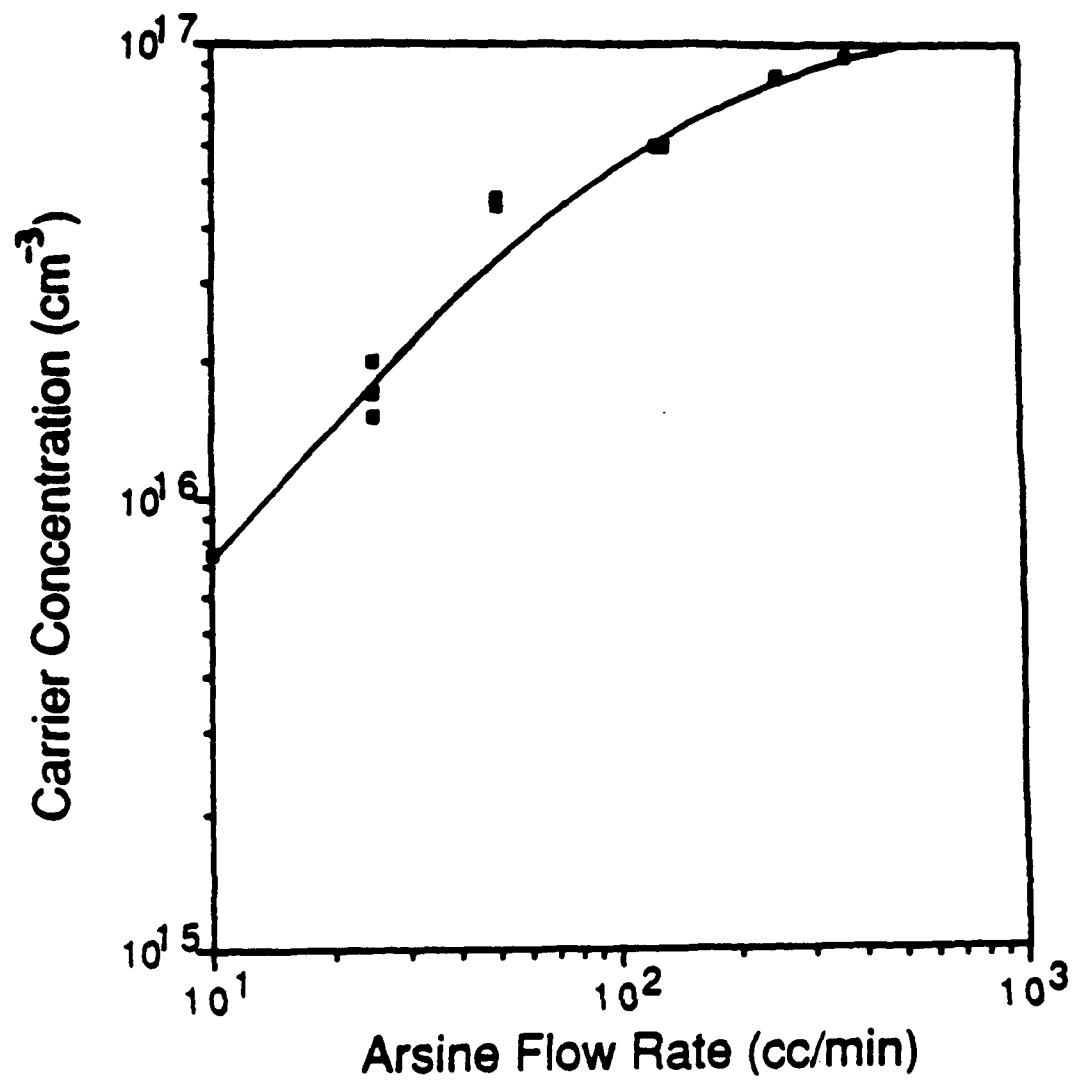


Fig. 2 Hole concentration vs.  $\text{AsH}_3$  flow rate.

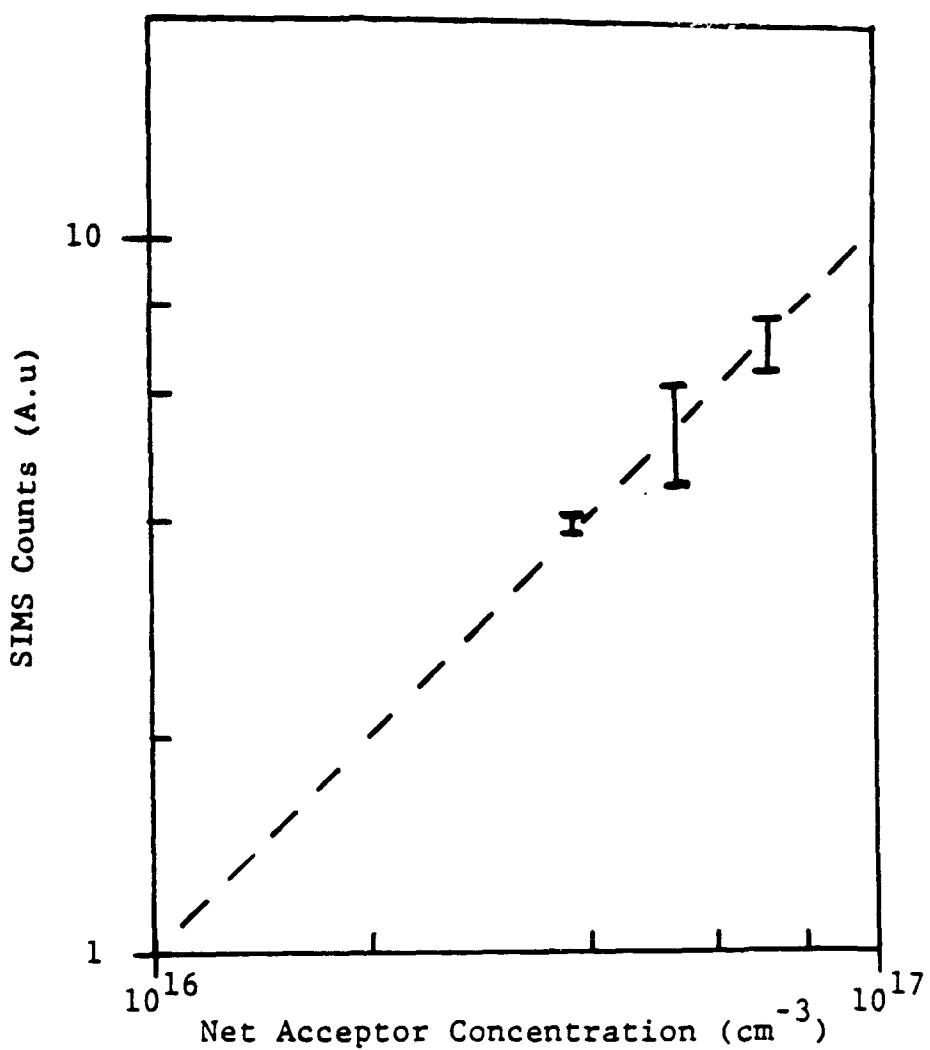


Fig. 3 SIMS count of arsenic vs. hole concentration.

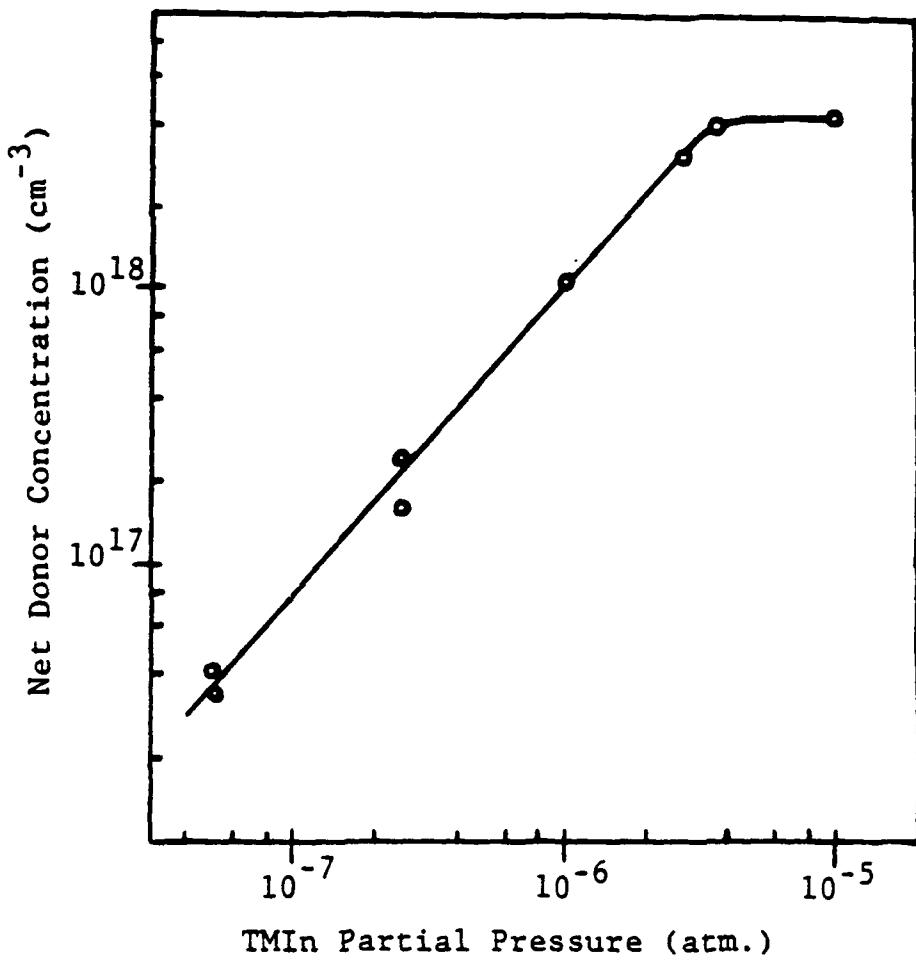


Fig. 4 Electron conentration vs. TMIn partial pressure.

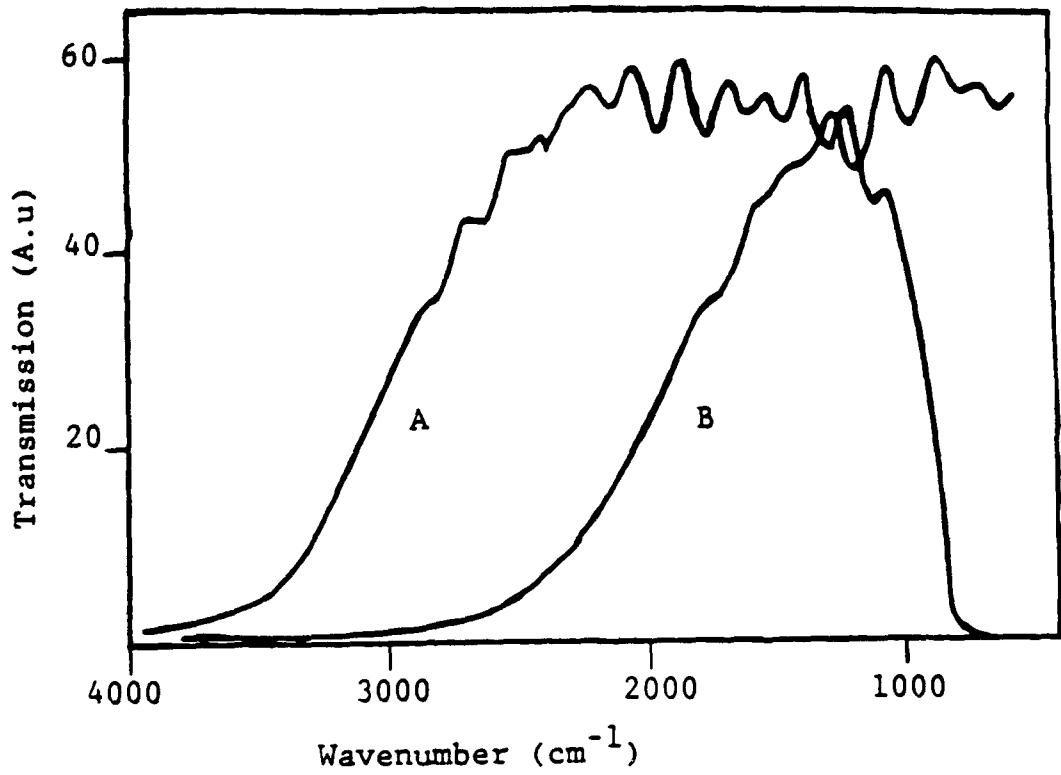


Fig. 5 FTIR characteristics for different doping concentrations.

TABLE  
 Carrier Concentration Dependence of Experimentally Determined  
 Optical Energy Gap

$x$	$E_g$ (meV)	$n$ ( $cm^{-3}$ )	$E_F - E_c$ (meV)	Theoretical	$E_{optical}$ (meV) Observed
0.17	113	$3 \times 10^{18}$	262	311	316
0.17	113	$5 \times 10^{18}$	319	372	372
0.23	200	$1 \times 10^{17}$	18	200	220
0.23	200	$4 \times 10^{18}$	259	390	384

↑  
 EDAX  
 VALUES.

**PHOTO-ASSISTED CHEMICAL BEAM EPITAXY OF  
CdTe AND HgCdTe ALLOYS**

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**EXTENDED ABSTRACT**

The range of bandgap energies and material properties required for complex infrared detector designs requires the development of II-VI material systems such as the ZnCdTe and HgCdTe alloys, and the ability to grow sophisticated structures in these material systems. Currently, molecular beam epitaxy is being investigated for this purpose, but the growth of high quality crystals and their reproducible doping is still a problem.<sup>1</sup> To overcome these limitations, a photon-assisted chemical beam epitaxy system has been developed. The advantage of this technique is that the use of hydride and/or metalorganic sources enables greater flexibility and more precise control to be achieved over the chemical reactions occurring during growth, as monomer, dimer, or tetramer species can be supplied to the growth surface depending on which is found to optimize the nucleation and growth processes. To implement this study, extensive modifications have been made to a Varian GEN II MBE system. These modifications consist of the development of a turbomolecular pumping system, new types of gas sources and injectors, and a Hg-vapor source.<sup>2,3</sup>

**Pumping System:** Because of the relatively high loads of toxic gases used in CBE, a specially designed pumping system was implemented to handle hazardous and corrosive organometallics, hydrides, and Hg vapor. Figure 1 shows a schematic representation of the pumping system, the main component of which is a Balzers MBE Series turbomolecular pump with a pumping speed of 1400 l/s for N<sub>2</sub> and approximately 1000 l/s for Hg. Gases exhausted from the turbomolecular pump pass into a cold trap operated at -60°C which is designed to condense the Hg vapor and minimize any contamination of the mechanical backing pump. Similarly, to minimize contamination of the turbomolecular pump due to hydrocarbon backstreaming, a micromaze oil vapor trap is included on the inlet of the backing pump.

The backing pump, an Alcatel 50 cfm Corrosion Series Pump, also uses inert gas ballasting to dilute and prevent condensation of the pumped vapors. The Alcatel pump exhausts into an Emcore toxic gas scrubber filled with a sulfur impregnated activated charcoal capable of absorbing up to 40 percent of its weight in Hg. This feature has no effect on the charcoal's ability to absorb organometallics and hydrides which can then be oxidized and disposed of in a controlled manner. As indicated in Figure 1, an array of valves enable various parts of this system to be isolated for removal of trapped vapors and the atmospheric pressure purging of both the pumping components and gas source lines.

Finally, a Varian cryopump is also attached to the system for removing Hg and organometallics from the growth ambient when needed. Provisions are made for hot gas purging of the cryopump using the gas purging system described above.

**Gas Sources:** The gas sources utilized in the CBE system are pressure controlled and can operate with inlet pressures on the order of one torr. Hence, the source gases can be directly injected without a carrier gas. This greatly simplifies gas source construction, minimizes the gas load on the pumping system, and makes it easier to maintain the beam fluxes in the molecular flow regime. This is especially important in the growth of Hg-based materials because of the large Hg fluxes required.

The pressure controlled vapor sources operate on the principle of choked viscous flow through an orifice and are similar in concept to a Hg source of this type currently in use in our laboratory.<sup>3</sup> The Te, Cd, and Zn sources operating on this principle use MKS Instruments 1150B flow controllers and are designed for the following source gases; diisopropyltelluride (DipTe), diethylcadmium (DeCd), and diethylzinc (DeZn). The DipTe (10 sccm f.s.), DeCd, and DeZn (5 sccm f.s.) flow controllers have repeatabilities of 0.2% and are configured to produce growth rates of up to 2  $\mu\text{m}/\text{hr}$ . The precision of the flow controllers is calculated to produce a stability in the Cd to Te ratio of approximately 0.1%. For  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  alloys with  $x = 0.2$ , this stability corresponds to a deviation in the  $x$  value of 0.0002, a factor 5-10 better than is currently available with conventional thermal sources.

**Dopant Source:** A p-type gas dopant source has also been designed, which operates on the same principle as the host gas sources. However, the design principles of the dopant source are even more severe as it must be able to accurately regulate flow rates that are four to eight orders of magnitude less than the host gas flow controllers. To achieve this level of control, an absolute pressure regulator is utilized, thus allowing control of the dopant gas at less than atmospheric pressure. The reduced pressure gas is then fed through a stepper motor driven leak valve which maintains the downstream pressure as measured by a high accuracy capacitance manometer. This controlled pressure exits through another leak valve (which acts as a variable orifice) and enters the CBE growth chamber. The sensitivity of the manometer and valve feedback system gives the dopant source a four order of magnitude dynamic range for a fixed orifice setting. Changing the orifice setting obviously allows the system to achieve an even greater dynamic range. Figure 2 shows a schematic of the dopant gas source. For the initial studies arsine was chosen as the dopant gas although, any of the organometallic As gases could be substituted when more fully developed. The pure arsine is contained in a small volume, low pressure bottle with a built-in flow limiting orifice, thus minimizing the safety hazards usually associated with arsine.

Injectors. To prevent gas phase reactions, separate injectors are used for the group II and group VI elements. This also enables optimization of the cracking conditions for each source gas. The group II injector uses a 3/4 in. o.d. high purity Ta delivery tube while the group VI utilizes a similarly sized pyrolytic boron nitride (PBN) delivery tube to avoid any reaction of Te with Ta. Both injectors are fitted with thermocouples to monitor the hot and cold zone temperatures and have individually designed boron nitride diffuser/nozzle elements to enhance the cracking of the metalorganic gases and increase flux uniformities. In particular, the group VI nozzle was designed to avoid the recombination of monomer Te into its dimer form, once it had been thermally dissociated from the metalorganic complex. Quadruple studies show that the monomer cracking efficiency is ~ 80% at low flow rates and decreases to ~60% for flow rates greater than 6 sccm.

Results: Using the full CBE capability of this system preliminary growth studies have been performed for HgTe,  $Hg_{1-x}Cd_xTe$  ( $0.10 < x < 0.30$ ) and  $Hg_{0.67}Zn_{0.33}Te$  epitaxial layers grown at temperatures between 160-195°C on both (001) GaAs and ZnCdTe substrates. For these growth runs accurate and reproducible substrate temperatures were obtained by using the Te-condensation technique developed at Georgia Tech.<sup>4</sup> Alloy compositions were obtained from room-temperature infrared transmission spectra. Low temperature (10-40K) Hall effect and resistivity data show that the HgTe and HgCdTe samples are n-type with electron concentrations between  $1 \times 10^{15}$  and  $3 \times 10^{14} \text{ cm}^{-3}$  and mobilities as high as  $3.3 \times 10^5 \text{ cm}^2/\text{Vs}$ . These preliminary results are very competitive with the best MBE data and demonstrate that hydrocarbons have little effect on the electrical properties even at very low growth temperatures. The rapid progress made with this system also demonstrates the precision of the new growth and temperature measuring techniques to control and establish optimum growth conditions. From these initial results we believe that CBE has the potential to solve many of the problems currently experienced by conventional growth technologies in obtaining abrupt heterointerfaces, precise stoichiometric adjustment and complex n- and p-type extrinsic doping profiles in II-VI semiconductor and superlattice systems.

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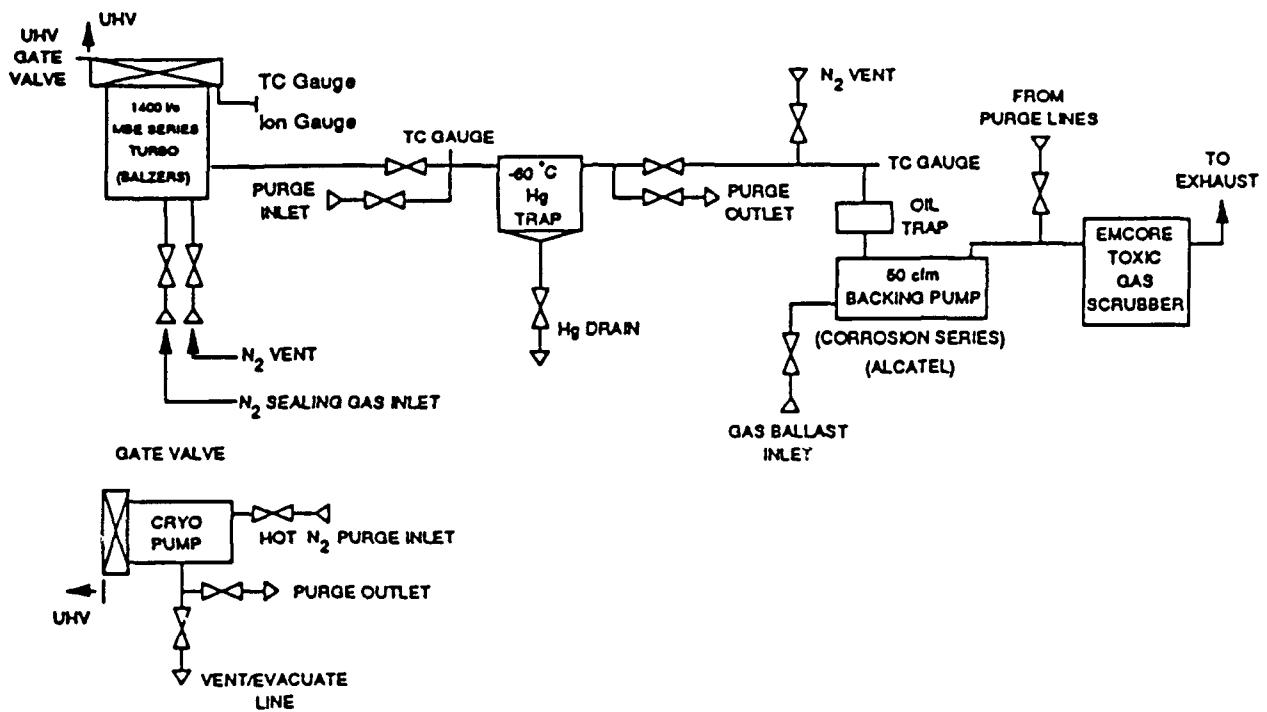


Figure 1. Schematic representation of CBE pumping system.

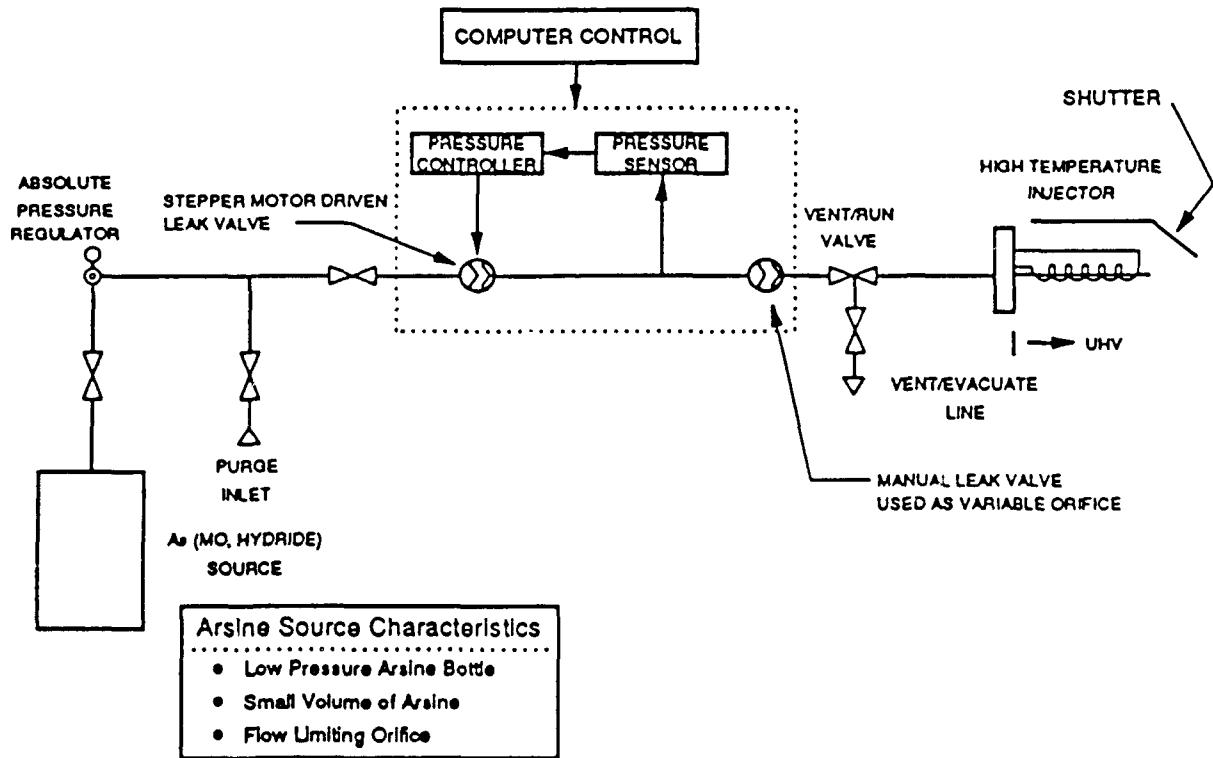


Figure 2. Schematic of arsenic gas dopant source.

## **In situ Analysis of ZnSe Growth by OM CVD Using X-ray Scattering**

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We have recently used grazing incidence x-ray scattering to do *in situ* analysis of the OMVPE growth of ZnSe on GaAs substrates. In this talk, we will discuss the establishment of an oxide free GaAs surface for epitaxial growth, and the initial stages of ZnSe growth using diethylselenium and diethylzinc precursors.

We find that surprisingly, there is a well-defined (2X1) reconstruction, apparently similar to that found during MBE growth, despite the presence of large amounts of organic by-products and a hydrogen atmosphere. This surface superstructure is stable over a wide range of growth conditions, with growth temperatures between 450 and 550 C, as well as Se/Zn ratios from 2 to 8. These results should give valuable insight into the mechanism of OMVPE growth.

# THE BIODEGRADATION OF GALLIUM ARSENIDE IC CHIPS AND WAFERS

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Project Scientist: Dr. Eric Eisenstadt

In the last decade, the electronics industry has emerged as one of the major forces in the world's economy. It grew 12% (\$770 billion) in 1988 and is forecast to show a consistent growth with a trillion dollar level attainable by 1992. In 1987, Gallium arsenide (GaAs) components were five percent of the total semiconductor device market (\$209 million). It is expected that this percentage will increase to 6 percent by 1991 (\$758 million). It is also expected that, GaAs wafers will account for 6 percent of the total merchant wafer consumption through 1991.

The GaAs market is being driven by the recent acceptance of GaAs ICs for mainframe computers, work stations and digital and microwave communication systems. GaAs materials quality, yield and availability have and will continue to improve. It is estimated, however, that more than 25% of the gallium used in the fabrication of gallium intermetallic compounds for solid-state diodes and other semiconductor devices is scrapped. Failed GaAs materials whether from undoped, unencapsulated wafers, doped wafers or fully mounted chips, range from 73% and must be discarded.

Recovery from scrap or secondary sources has been very small. According to a preprint from the 1989 Bureau of Mines Minerals Yearbook entitled Gallium, Eagle-Picher chemically recovers and refines gallium from primary and secondary materials at its plant in Quapaw, OK. Recapture Metals Inc., Blanding, UT, recovered gallium from GaAs scrap using high concentration acid solvents. Lastly, Sulzer Brothers constructed a chemical gallium extraction plant at Kaiser Aluminum & Chemical's alumina refinery in Gramercy, LA in 1988. These systems, however, do not recover or safely remove the arsenic or other metal materials.

Biodegradation (bioleaching--solubilization of minerals via microorganisms) has been patented and used in conjunction with traditional mineral and element extraction for several decades in the United States. Traditional biosolubilization work has centered on sulfide-bearing ores. In Gallium bioleach work, Lundgren, Torma, Karaivko and Ivanov reported that *Thiobacillus ferrooxidans* (37°) was used to oxidize gallium sulfide ( $\text{Ga}_2\text{S}_3$ ) to gallium sulfate ( $\text{Ga}_2(\text{SO}_4)_3$ ) and to leach gallium non-ferrous metals.

Proprietary materials, scrap or secondary sources are not traditionally recycled, with a multimillion dollar loss of gallium, gold and silver. Our laboratories have shown that bacteria found to be successful in a three year gallium bioleach ore research and development project with the Air Force can successfully biodegrade scrap or secondary GaAs IC chips and wafers (Aesar, Tandy, National Semiconductor and Zilog). After solubilization, the gallium, copper, tin and arsenic can be recovered. The unaltered gold wire and silver crystals are deposited. Follow-on work with indium and copper arsenides as well as selenide are also promising. With this new biodegradation recovery process, it is believed that additional, inexpensive U.S. assets could be recycled and possible hazardous waste situations could be eliminated.

# **Detailed Models of Compound Semiconductor Growth by MOCVD**

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The current state of metalorganic chemical vapor deposition (MOCVD) reactor modelling is reviewed with emphasis on two- and three-dimensional transport phenomena combined with gas-phase and surface reactions underlying the growth of GaAs and related compound semiconductors. Physicochemical models are presented and shown to gain insight into the fundamental mechanisms governing growth uniformity, impurity incorporation, and compositional variation across heterojunctions. Particular attention is given to the understanding the development of fully three-dimensional flows and to the interaction between transport and chemical reaction processes. The classical vertical and horizontal reactor configurations are used as example reactor systems to illustrate key modelling issues.

In the case of vertical reactors, finite element models are used to explore parameters (e.g. reactor geometry, substrate rotation, wall temperature, and pressure) governing the flow behavior. The simulations show that good film thickness uniformity and sharp compositional gradients across heterojunctions can be achieved through system modifications such as a wide reactor inlet, substrate rotation and a short distance between inlet and substrate. The first fully three-dimensional finite element computations of non-axisymmetric flows in vertical MOCVD reactors are presented. These asymmetric flows readily develop for an inlet tube placed off-axis or in the presence of azimuthal temperature variations on the susceptor or reactor walls. The analysis indicates that non-axisymmetric solutions only occur in symmetric reactor enclosures under conditions where multiple stable flows are possible. Since the occurrence of multiple flows diminishes with pressure and reactor height, it is possible to realize axisymmetric flow fields in reduced pressure, low height to diameter aspect ratio MOCVD reactors.

We demonstrate the significant impact of wall heat transfer on flow phenomena in horizontal reactors, in particular with respect to the "cold finger" phenomena. Three-dimensional simulations are used to predict quantitatively laser holography observations of cold finger and convection roll phenomena in horizontal reactors. The thermophoretic transport of particles, generated in the deposition processes or intentionally added for flow visualization purposes, is also modelled and the results are in excellent agreement with experimental data. The computations demonstrate that the thermophoretic force causes particles to deviate from the actual fluid path in regions of large thermal gradients, i.e. near the substrate. Besides the detrimental effects to flow visualization, the thermophoretic transport plays an advantageous role in MOCVD processes by forcing particle contaminants away from the growing film.

Because of the complexity of the transport phenomena and the number of reactions involved in detailed MOCVD reactor models, previous models have focused on either transport processes or chemical mechanisms. We present a model encompassing both chemistry and transport. This model is based on a detailed kinetic model for epitaxial growth of GaAs from trimethylgallium and arsine with fluid flow and heat transfer models for typical horizontal and vertical MOCVD reactor configurations. The deposition mechanism involves a large number of gas-phase and surface reactions. The influence of the crystallographic orientation of the substrate on the surface reactions is included in the kinetic model along with a new mechanism for carbon incorporation based on two-site adsorption of carbene containing gallium species. Reaction rate parameters for fundamental reaction steps (e.g. decomposition, recombination, adsorption, surface reaction, and desorption) are estimated from thermochemical data and existing experimental observations. In addition, values of unknown reaction parameters are resolved by simulations of reported decomposition and growth data. The use of this detailed chemical mechanism makes it possible to evaluate the relative importance of different reaction pathways. The growth rate predictions are shown to be very sensitive to surface reactions but not to the details of the gas-phase chemistry. However, the complete reaction mechanism is critical to the simulation of carbon incorporation.

The model predictions are in good agreement with conversion and product distribution data for trimethylgallium pyrolysis in different carrier gases in hot isothermal tubes. In addition, the model predicts quantitatively GaAs growth rates in horizontal and vertical reactors and qualitatively carbon incorporation trends with temperature, pressure and V/III ratio. The computations show that the wall

temperature plays a critical role in controlling uniformity, particularly in horizontal systems with sloped susceptors.

In addition to considering the unintentional incorporation of carbon, the intentional doping of GaAs by silane and disilane is considered. It is demonstrated that by using a detailed model with kinetic parameters for the silane and disilane system, it is possible to predict and explain observed variations in silicon doping efficiency.

The results demonstrate that is feasible to predict not only growth rates but also impurity incorporation levels if chemical kinetics is combined with accurate models of MOCVD transport processes. Finally, extensions of the detailed modelling approach to other MOCVD systems, in particular the simulation of growth of ternary and quaternary compounds, is discussed along with the use of the models in the further development of MOCVD reactor technology.

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## Gas Phase Probes of Gallium Arsenide Cluster Chemistry

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Extensive efforts over the past few years have been devoted to the preparation and study of bare, unsupported clusters of semiconductors such as silicon and gallium arsenide. The aim of this work is to provide a molecular-scale testing ground for the development of a detailed fundamental understanding of the surface chemistry of these materials. Using one of the most powerful of these new techniques, Fourier transform ion cyclotron resonance (FT-ICR), we have been exploring the chemistry of small clusters of gallium arsenide levitated in a magnetic field in a ultrahigh vacuum. The results indicate that clusters with eight or more atoms behave very much like the bulk GaAs surface in two respects: (1) the surface restructuring has removed dangling bonds, sweeping out surface states from the band gap region, and (2) the effect of this restructuring appears to have activated the surface arsenic atoms as Lewis acid sites for the chemisorption of such species as ammonia. Even with as few as eight atoms, these clusters appear to have adopted structures which alternate the gallium and arsenic atoms as much as possible. This provides a considerable simplification to these species as molecular scale models of the bulk GaAs surface.

Information concerning the absence of dangling bonds has come from two experiments. In one the photoionization efficiency of a wide range of neutral gallium arsenide clusters was measured at a number of photon energies. The remarkable result was that all clusters in the 2-30 atom size range with an even number of atoms were observed to have an ionization potential (IP) above 6.4 eV, while all the odd clusters had an ionization potential below 6.4 eV. This even/odd oscillation in ionization potential persisted even over a broad range of Ga/As compositions in the  $\text{Ga}_x\text{As}_y$  clusters. The only convincing explanation yet offered for this result is that the clusters have managed to restructure so that all surface "dangling bond states" have been tied up, leaving all the even numbered clusters in closed-shell singlet ground states. The other information has come from a series of detailed measurements of the ultraviolet photoelectron spectrum (UPS) of the mass-selected cold negative clusters,  $\text{Ga}_x\text{As}_y^-$ . The lowest energy photodetachment threshold measured from these UPS data provide an estimate for the vertical electron affinity (EA) of the corresponding neutral cluster. The clear result from these measurements was that throughout the 2-50 atom size range, these clusters display an even/odd alternation in the electron affinity. For the even-numbered clusters this suggests a band gap exists in the surface density of states of roughly 1 eV.

Surface chemical probes of these gallium arsenide clusters have been obtained on a specially-designed fourier transform ion cyclotron resonance (FT-ICR) apparatus which features direct injection of the clusters prepared in a supersonic beam. The most interesting results found so far concern the reactivity of the mass-selected positive cluster ions toward chemisorption of ammonia. Here the bare cluster ion is levitated in a strong magnetic field in an ultra high vacuum. Chemistry evolving on the surface of the cluster is monitored by coherent excitation of the cyclotron motion of the resultant cluster products. Given the extremely high mass resolution of the FT-ICR it is possible to determine the relative abundance of the various compositions possible for a particular cluster size (ie the x/y ratio for a particular value of  $n=x+y$  in clusters of formula  $Ga_xAs_y^+$ ). After thermalization and subsequent exposure to several thousand collisions with ammonia the relative reactivity of these different compositions can be measured. The key result is that all clusters with 8 or more atoms are found to be most reactive at the 1:1 stoichiometric composition. This is true for all the larger clusters even though it is clear in many cases that there are several structural isomers present.

Although there is much yet to be done with such surface chemisorption experiments, this initial striking result is already quite provocative. It indicates that the active site for initial chemisorption of ammonia must involve both gallium and arsenic. The simplest (and currently the only) convincing explanation is that already at these small cluster sizes the gallium and arsenic atoms have arranged in a way that alternates the arrangement of atoms as much as possible. The interaction with adjacent arsenic atoms has promoted the gallium atoms into effective Lewis acid sites for the initial attack of the  $NH_3$ .

Together with the IP and EA measurements these chemisorption results indicate that the  $Ga_xAs_y$  clusters with  $x+y>8$  are already much like the bulk surface of gallium arsenide. On the bulk surface it is now generally agreed that restructuring leaves the surface gallium and arsenic atoms each 3-coordinated with a lone pair of electrons on the arsenic and a vacant p orbital on each gallium. Similar surface restructuring of the  $Ga_xAs_y$  clusters would produce the IP/EA and chemisorption results we have observed.

Stimulated by these new experimental results, detailed calculations of these gallium arsenide clusters are now in progress in a variety of laboratories (including our own). Initial results agree that the clusters do alternate the gallium and arsenic atoms around the structure as much as possible. Further detailed experimental and theoretical studies of these isolated pieces of the gallium arsenide surface may therefore lead to a much deeper understanding of gallium arsenide surface chemistry.

Photodecomposition of Organometallic Compounds at 193 nm

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Chemical vapor deposition may be achieved by the pyrolysis or photodecomposition of appropriate organometallic compounds. In this investigation the goal is to evaluate the photodecomposition mechanism of trimethyl gallium (TMG) and trimethyl arsine (TMA) in the vacuum ultraviolet, specifically at 193 nm, the ArF laser line.

The sharp absorption peak of  $\text{CH}_3$  at 216.4 nm furnishes a convenient analytical approach for the quantitative assessment of the temporal methyl concentration subsequent to the laser pulse. Chromatography of the end products is used to confirm the optical results. A comparison with an actinometric standard such as acetone, with a known quantum yield from methyl of 2 should, by comparison with the organometallic compound, lead to the appropriate quantum yield for the organometallic. In the case of TMG, a discrepancy was found between the ethane found chromatographically and that expected on the basis of the optical methyl analysis. The latter was considerably higher. This result was attributed to a radical containing gallium moiety from the photolysis that absorbed where methyl does, at 216.4 nm.

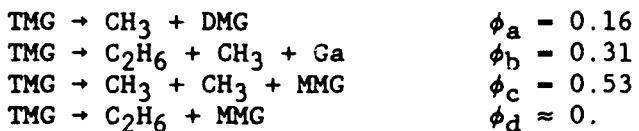
A method based on isotope distribution was devised to evaluate the photochemical decomposition mechanism for TMG<sup>1</sup>. This involved the photolysis of a mixture of completely deuterated acetone with TMG. The  $\text{CD}_3$  and  $\text{CH}_3$  produced in the decomposition recombine to give completely deuterated, half deuterated, and nondeuterated ethanes. The ratio  $(\text{CH}_3\text{CD}_3)^2/((\text{C}_2\text{H}_6)(\text{C}_2\text{D}_6))$  must equal 4 if no source of ethane extraneous to methyl recombination is present. For the acetone-d6 and TMG system it was found, however, that the above expression did not yield 4. It was concluded that in the TMG photolysis at 193 nm there is an intramolecular ethane elimination channel.

If we define  $P_D$ ,  $\epsilon_D$ ,  $P_H$  and  $\epsilon_H$  as the pressures and the absorption coefficients of the acetone-d6 and TMG respectively and define Q as the quantum yield of 'total' methyl, F as the fraction of 'total' methyl that is free, (1-F) the fraction that is produced intramolecularly, then the following two equations can be derived:

$$X = Q \cdot F = \frac{[\text{CH}_3\text{CD}_3] \epsilon_D P_D}{[\text{C}_2\text{D}_6] \epsilon_H P_H} ; \quad Y = \frac{4 \epsilon_D P_D [\text{C}_2\text{H}_6]}{\epsilon_H P_H [\text{CH}_3\text{CD}_3]} - Q + \frac{2(1-F) \epsilon_D P_D}{F \epsilon_H P_H}$$

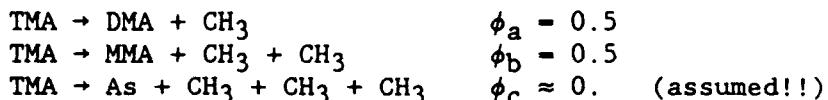
If  $\text{CD}_3$  reacted with TMG, if F and Q were functions of pressure, or if there were different production rates for  $\text{CH}_3$  and  $\text{CD}_3$ , the above model would be invalid. However, there is strong evidence that none of these effects occur.

From the measurements and use of the above equations it is concluded that Q=2.15 and F=0.71 from which the following quantum yields can be derived (DMG=dimethyl gallium, MMG=monomethyl gallium),



The absorption at 216.4 nm attributed to a methyl gallium type radical was found to have an absorption peak at 220 nm as well. This intermediate, postulated to be the dimethyl gallium radical, is most probably a precursor to gallium metal formation.

The photodecomposition of TMA is simpler than that of TMG. Trimethyl arsine was photodecomposed at 193 nm, the course of the reaction being monitored by the observation of methyl formation and decay. The quantum yield for methyl formation was found to be 1.5. The only product found with gas chromatography was ethane. This correlated well with the  $\text{CH}_3$  as determined by optical absorption. The methyl decay, determined optically, shows the initial formation and second order decay but even after a period of milliseconds the signal does not revert to the base line. This suggests the formation of relatively stable species such  $\text{As}(\text{CH}_3)_2$  and  $\text{As}(\text{CH}_3)$ . There is no indication of any intramolecular elimination processes as in the case of TMG. On this basis the following quantum yields are derived.



Further experiments on TMA involving isotopic analysis are in progress. Results of these will be more sensitive for the detection of very small amounts of intramolecular ethane formation.

Present protocols are capable of determining quantum yields for dissociation of a large number of organometallic compounds. Such data provide the necessary first step for unravelling the total reaction kinetics in these potentially complex kinetic systems and hence the complete understanding of the CVD (photochemical as well as thermal) processes.

#### REFERENCE:

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## **ABSTRACT**

### **MANUFACTURING ISSUES IN MOCVD COMPOUND SEMICONDUCTOR TECHNOLOGY**

**BY**

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Manufacturing applications utilizing compound semiconductor epitaxial structures have been increasing in the optoelectronics, microwave and energy conversion device areas. There is also recent activity suggesting that digital IC manufacturers are evaluating epitaxial structures on an experimental basis.

This talk will focus on issues of system and reactor design which arise from manufacturing considerations. Specifically, these include single vs. multiwafer, batch size, and reactor cycle time. In addition, system design features such as multi-chamber multi-function configurations, process monitoring and control system technology will be discussed. The questions of designing for reliability and reproducibility and generating meaningful statistical data are central to producing hardware which is compatible with a manufacturing environment. This requires the close collaboration of equipment manufacturers and customers. Since the customer-vendor relationship is a key ingredient for the success of both parties in this highly competitive area, it is important to examine the extent to which this collaboration is allowed to occur.

## ARSINE GENERATOR SYSTEM

The arsine generator system provides a safe alternative to compressed gas cylinders without sacrificing arsine purity.

The arsine generator system fits into a standard compressed gas cylinder cabinet. The generator has a five pound arsine capacity. A replaceable stainless steel container holds the arsine source material. Once this material is depleted, the container is exchanged. The container is easily attached to the system with VCR connectors.

The arsine purity produced by the generator exceeds SEMI Specification C3STD 2-81 and meets or exceeds that available from compressed gas sources. The principle impurity is water vapor (typically 80 ppb) which is removed with a series of molecular sieves.

The generator can be operated to provide either 85% arsine in hydrogen at low flow rates (up to 90 cc/min at 30 psig) or 10% arsine in hydrogen (up to 750 cc/min at 30 psig).

The system is operated from a lap-top computer connected to both analog and microprocessor based controls. System evacuation, purging, and operation are automatically controlled.

### System Components

The standard arsine generator system consists of the following components mounted on a frame which fits into a standard gas cabinet.

-Electrochemical arsine generator

-Electropolished manifold with air actuated bellow valves, molecular sieves, and valve controller. All manifold fittings are welded or attached with VCR fittings.

Rack mounted outside the cabinet:

-DC power supply, analog and microprocess base system controller

The control system also attaches to an MDA arsine monitor for automatic shut-off if arsine is detected in the cabinet.

### Arsine Specifications

Arsine purity meets or exceeds electronic grade arsine (SEMI Specification C3STD 2-81)

Water	<3 ppm
Oxygen	<5
Nitrogen	<5
Carbon oxides	<2
Hydrocarbons	<1
Other hydrides	ND

### System Requirements

115 V AC, 60 cycle 15 amp  
 Gas cabinet  
 Arsine regulator  
 Hydrogen cylinder for purge and flow operation  
 Vacuum pump for initial evacuation (required at container change)

### Ordering Information

ASGS-1 Arsine Generator System,  
 5 lb arsine capacity  
 ASGS-2 Arsine Generator System,  
 10 lb capacity

### Options:

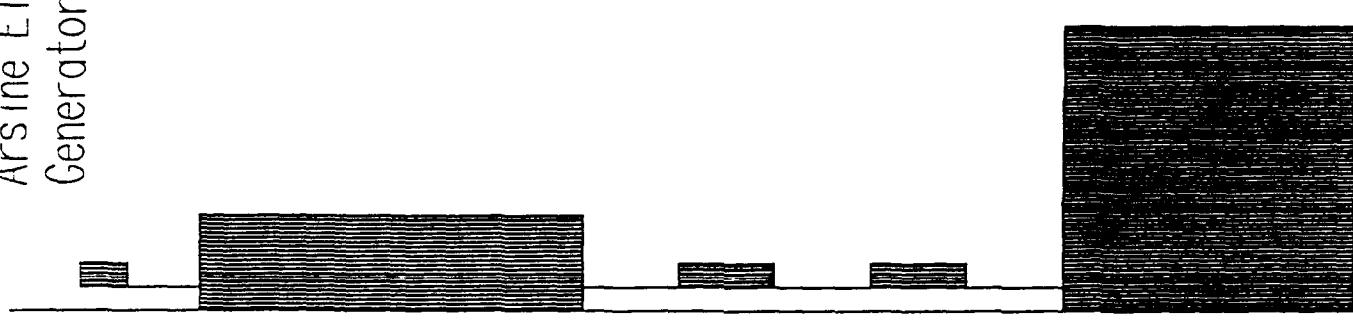
- O1-Tribodyn 30 vacuum pump
- O2-Gas Cabinet
- O3-Oxygen sensor
- O4-Arsine mass flow controller
- O5-MDA Arsine detector
- O6-220 V power

### For more information contact:

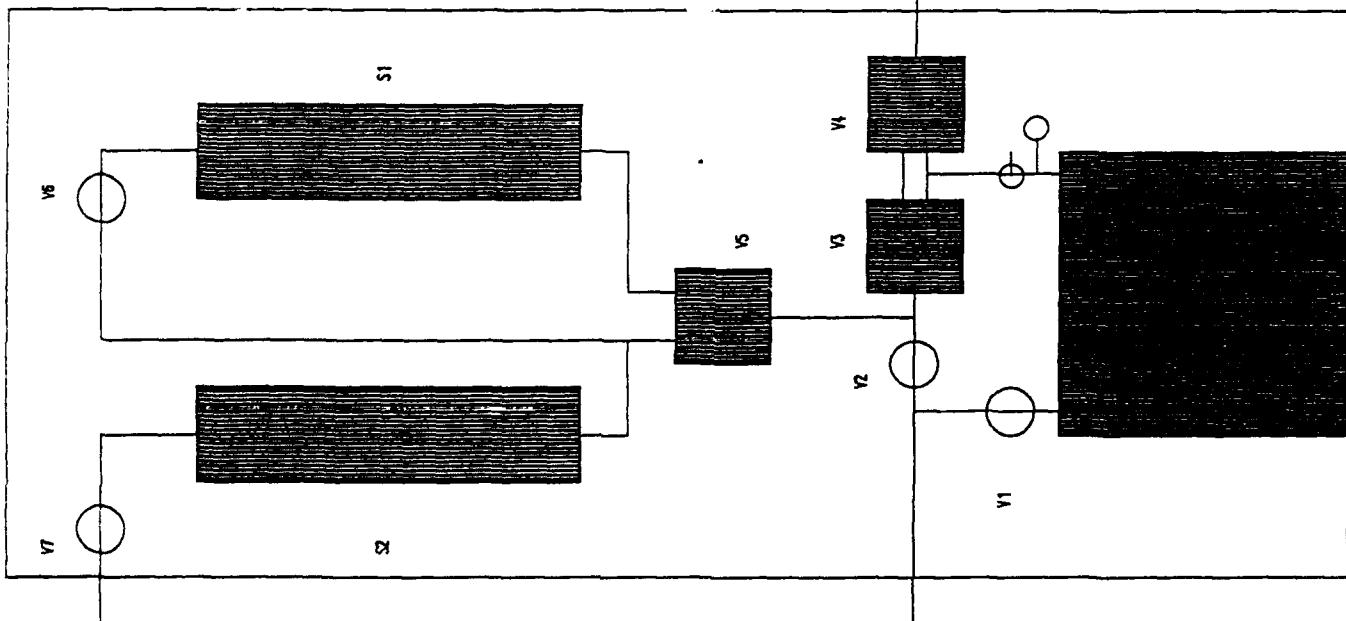
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# Arsine Electrochemical Generator System



Value



(48" high, 18" wide)

## ARSINE GENERATOR SYSTEM

### Beta Site Unit

#### Price List

ASGS-1 Complete 5 lb capacity arsine generator system,	\$ 45,000
ASGS-2 10 lb capacity system,	\$ 59,000

ASGS-C1 5 lb capacity container exchange source,	\$ 2,500
ASGS-C2 10 lb capacity exchange source	\$ 4,800

#### Options:

O1-Tribodyn 30 vacuum pump,	\$ 6,900
O2-Gas Cabinet,	request
O3-Oxygen sensor	"
O4-Arsine regulator	"
O5-Arsine mass flow controller	\$ 4,600
O6-MDA Arsine detector,	\$ 3,600

Prices FOB Princeton, NJ. Prices subject to change

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